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Leaves Extract of *Cajanus Cajan* (Pigean pea) as Corrosion Inhibitor for Mild Steel in Simulated Seawater Environment

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Abstract— *There is a new direction in research towards the use of plant of natural origin as corrosion inhibitors for metals and alloys. Sequence to this, the corrosion inhibition of mild steel in 3.5% sodium chloride (NaCl) solution by cajanus cajan leaves extract has been 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 increases with the 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 was calculated and these thermodynamic parameters show strong interaction between inhibitor and mild steel surface.*

Keywords— *Mild steel, Corrosion inhibition, weight loss, Activation energy, Adsorption isotherms.*

I. INTRODUCTION

Plants of natural origin are viewed as an incredibly rich source of chemical compounds that can be extracted by simple methods with low cost and are biodegradable in the environment. Presently, there is an increasing awareness of protecting the materials 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 steels in acidic/alkaline media and have been reported, such as *Aquilaria crassna* [1], *Portulaca oleracea* [2], *Tagetes erecta* [3], *Aloe vera* [4, 5], *Justicia gendarussa* [6], *Phyllanthus amarus* [7]. It was found that the inhibition performance of plant extract is normally ascribed to the presence in their composition 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 N, S, O atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers. 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 [8].

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 cajanus cajan is a flat, straight, pubescent pod, 5-9 cm long and 12-13mm wide. Pigean pea is used as a contour hedge in erosion control [9]. The leaves extract of pigean pea is used as corrosion inhibitor in the current study been a byproduct, waste, biodegradable, ecofriendly.

II. EXPERIMENTAL

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 desiccators before use as described elsewhere [9].

TABLE 1:

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

Cajanus cajan leaves was collected from a garden, washed and shade dried. It was later pulverized with mortar and100g out of it was soaked in distilled water (1000ml) 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 ^{0}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.

2.2 Weight Loss Technique

The experiment was carried out at 30 ^{0}C and 60 ^{0}C 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 difference in weight was taken as weight loss. The corrosion rates (CR) was calculated from the weight loss using Equation 1, the inhibition efficiency (IE%) and surface coverage (Ɵ) were calculated using Equations 2 and 3 as follows:

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

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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)

$$IE\% = 1 - \frac{W_1}{W} \times 100\ \% \quad (2)$$

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

$$\theta = 1 - \frac{W_1}{W} \quad (3)$$

III. Results and Discussion

3.1 Phytochemical Screening of Cajanus Cajan Leaves (CC)

The phytochemical screening of methanol 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 methanol extract of *cajanus cajan* extracts, hence the inhibition efficiency of methanol extract of plant may be attributed to the phytochemical constituent of the extract.

TABLE 2: Qualitative phytochemical analysis of *cajanus cajan* (Methanol)

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

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

3.2 Weight Loss Measurements

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 30^0C, the corrosion rate for the control is 0.5604 mg/cm^2 hr but this value was reduced to 0.0856 mg/cm^2 hr in the presence of inhibitor. Similar trend was observed at 60^0C . 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 [10]. The least corrosion rate was obtained at 30^0C and at 250 mg / l concentration. However, as the temperature increased to 60^0C, 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 environment.

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 30^0C, maximum inhibition efficiency of 84.73 % was obtained at 250 mg/l inhibitor concentration. The reduction in inhibition efficiency at 60^0C 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 coverage.

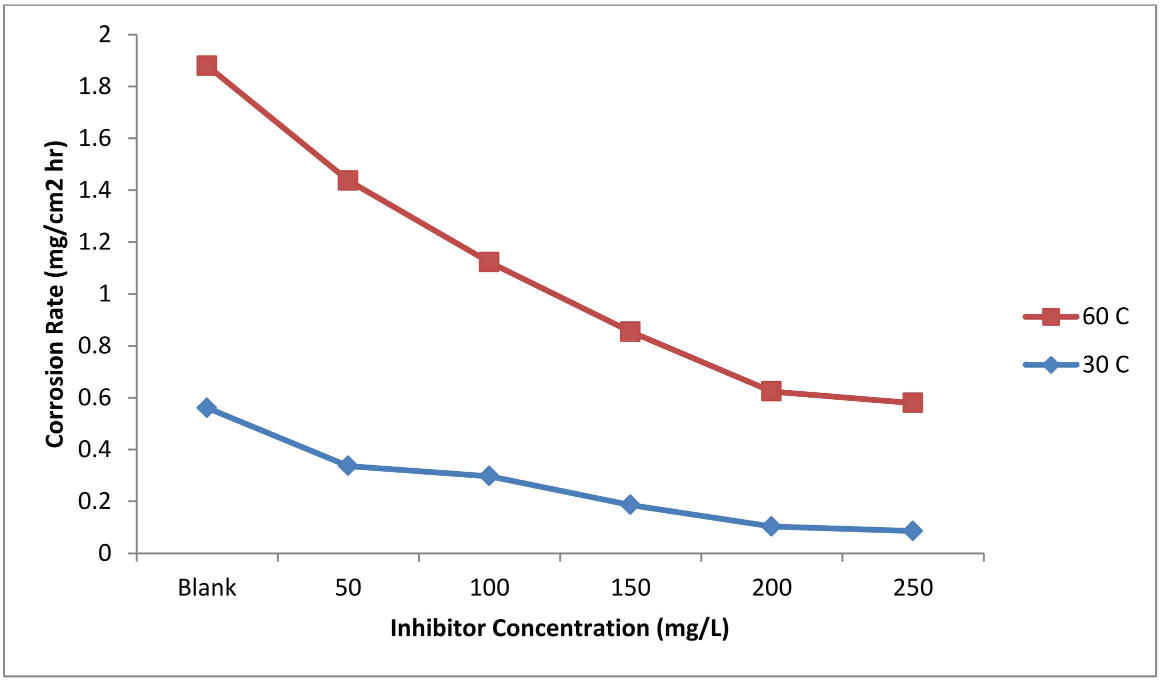

Figure 1: Corrosion Rate of Mild Steel in 3.5 wt.% NaCl solution in the absence and presence of *cajanus cajan* leaves extract at various temperatures

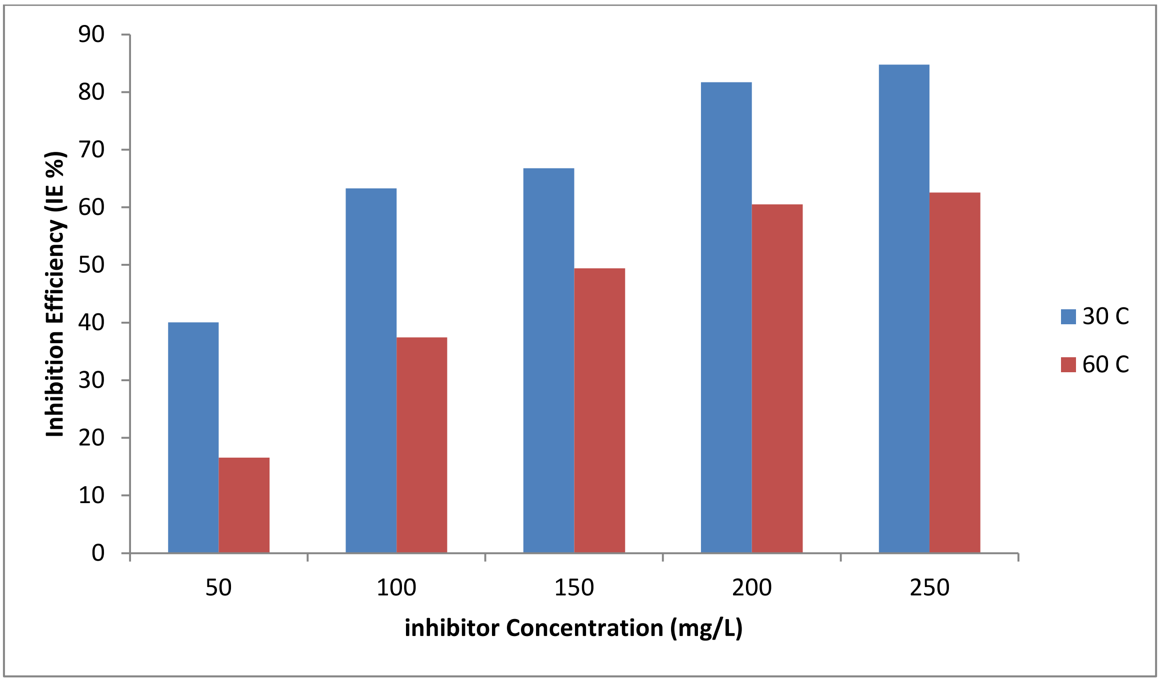

Figure 2: Inhibition Efficiency of Mild Steel in 3.5 wt.% NaCl solution in the absence and presence of *cajanus cajan* leaves extract at various temperatures

TABLE 3: Corrosion Rate of Mild Steel in 3.5 wt.% NaCl solution in the absence and presence of *cajanus cajan* leaves extract at various temperatures

Inhibitor Concentration (mg/l)	CR at 303 k (mg/cm^2 hr)	Inhibition Efficiency IE%	Surface Coverage (Ɵ)	CR at 333 k (mg/cm^2 hr)	Inhibition Efficiency IE%	Surface Coverage (Ɵ)
Blank	0.5604	_	_	1.3192	_	_
50	0.3362	40.01	0.4001	1.1004	16.59	0.1659
100	0.2059	63.26	0.6326	0.8251	37.45	0.3745
150	0.1861	66.79	0.6679	0.6673	49.42	0.4942
200	0.1024	81.73	0.8173	0.5211	60.50	0.6050
250	0.0856	84.73	0.8473	0.4936	62.58	0.6258

3.3 Effect of Temperature

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 range of temperature 30^0C to 60^0C in the absence and presence of *cajanus cajan* leaves extract at optimum concentration and over the exposure time using the Arrhenius state equation as shown in Equations (4) and (5) [11].

$$\log CR = \log A - Ea/2.303RT \quad (4)$$

$$\log\left(\frac{CR}{T}\right) = \{\log(R/NA\,h) + \Delta Sa/2.303R\} - \Delta Ha/2.303RT \quad (5)$$

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 4, 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 can be calculated.

From Equation (5), plot of $Log\ CR/T$ 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 enthyalpy and entropy of activation for the corrosion process can be calculated. Values of Ea, ΔSa, and ΔHa are presented in Table 4. 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 [12]. 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.

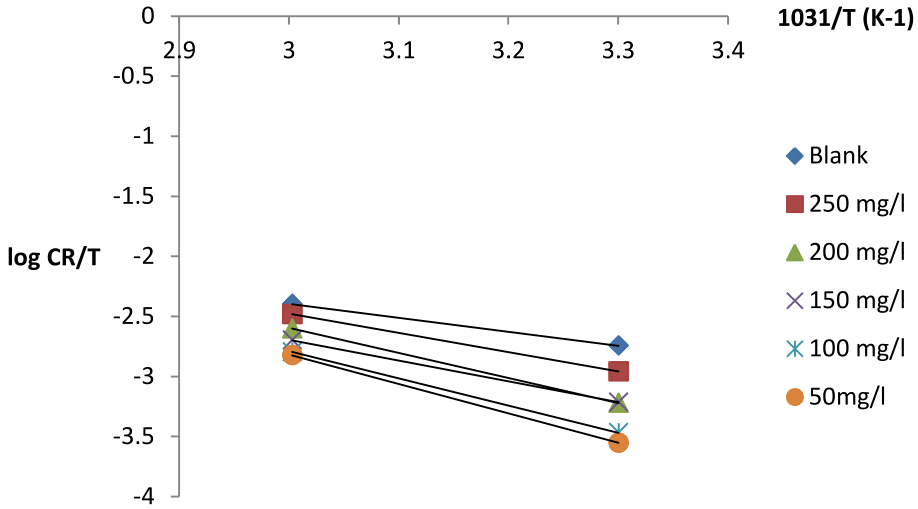

Figure 3: Arrhenius plots for the mild steel dissolutioin in the absence and presence of *cajanus cajan* leaves extract

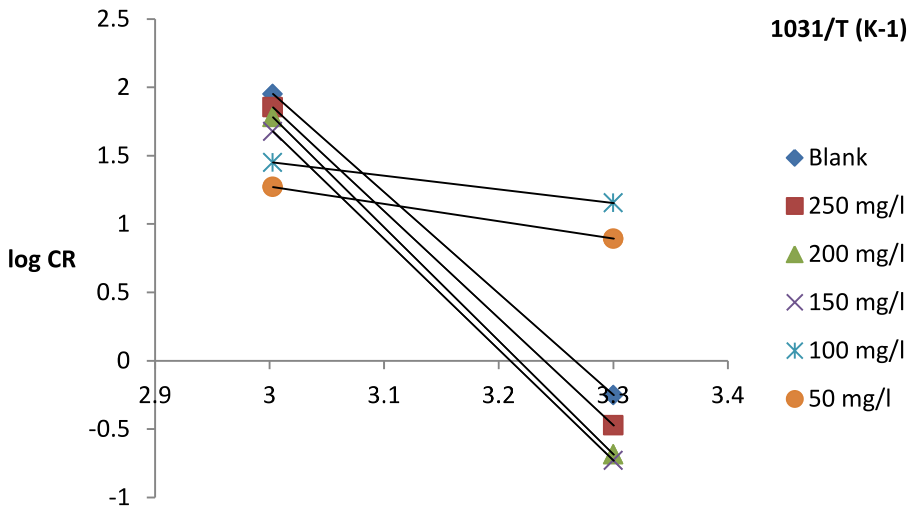

Figure 4: Activation energy plots for the mild steel dissolutioin in the absence and presence of *cajanus cajan* leaves extract

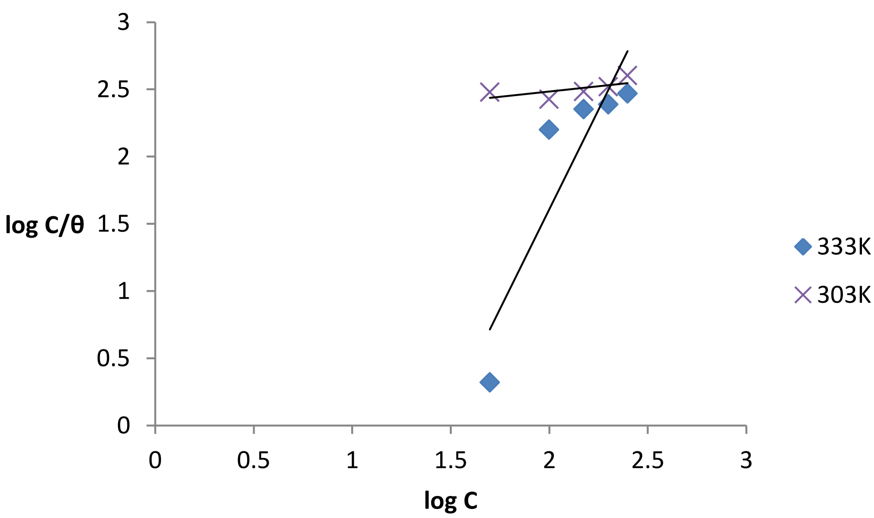

Figure 5: Langmuir adsorption isotherm

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TABLE 4: Activation parameters for the mild steel dissolution in the absence and presence of *cajanus cajan* leaves extract

Inhibitor Conc. (mg/l)	Ea (kJ/Mol.)	∆Ha (kJ/Mol.)	∆Sa(kJ/Mol. / k)	Qads (kJ/Mol.)
Blank	23.93	22.33	176.55	__
50	48.99	46.93	110.77	35.18
100	45.49	43.31	121.13	29.54
150	35.71	33.20	149.66	20.11
200	38.81	39.90	127.66	29.97
250	33.16	30.71	152.93	33.54

3.6 Adsorption Isotherm

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

$$\frac{c}{\theta} = \frac{1}{K} + c \quad (4)$$

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 [13]. Taking the

$$log\frac{c}{\theta} = c + 1/k \quad (5)$$

Logarithm of equation 4, equation 5 is obtained. The plot of log c / Ɵ 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.

3.7 Thermodynamic Studies

Thermodynamic parameters play an important role in studying the inhibitive mechanism. The standard adsorption free energy ($\Delta G^o{}_{ads}$) was obtained according to [12].

$$\Delta Gads = -RT\ln(55.5\ K) \quad (6)$$

Where R is the molar gas constant, T is the temperature in Kelvin, 55.5 is the molar concentration of water and K_{ads} = Ɵ/(1 –Ɵ) C.

Calculated values of the free energy are presented in Tables 5. Generally, values of $\Delta G^o{}_{ads}$ 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 (chemisorptions) [14]. 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 [15].

TABLE 5: Langmuir adsorption isotherm parameter

Temperature (k)	R^2	ΔG_{ads} (kJ/Mol.)
303	0.456	- 12.07
333	0.800	- 13.80

IV. 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. The mechanism of physical adsorption was proposed from the results obtained for the values of activation energy, enthalpy and free energy changes.

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Conflict of Interest

The authors did not declare any conflict of interest.

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