Corrosion Inhibition Performance of Lignin Extract of Sun Flower (*Tithonia Diversifolia*) on Medium Carbon Low Alloy Steel Immersed in H_2SO_4 Solution

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Abstract

The inhibition potentials of lignin extract of sun flower was investigated by evaluating the corrosion behaviour of medium carbon low alloy steel immersed in 1M H_2SO_4 solution containing varied concentration of the extract. Mass loss, corrosion rate, and adsorption characterization were utilized to evaluate the corrosion inhibition and adsorption properties of the extract. The results revealed that the lignin extract is an efficient inhibitor of corrosion in mild steel immersed in 1M H_2SO_4. The corrosion rates were observed to decrease with increase in concentration of lignin extract but increase with temperature. The activation energies and the negative free energy of adsorption obtained from the adsorption studies indicate that the lignin extract is physically adsorbed on the surface of the steel and that the adsorption is strong, spontaneous and fit excellently with the assumptions of the Langmuir adsorption isotherm.

Keywords

Lignin; Corrosion inhibition; Mass loss; Low alloy steel; Adsorption; H_2SO_4; Activation energy; Langmuir isotherm.

Introduction

The corrosion of engineering materials is known to lower performance efficiency and lead to reduced service life, in severe cases it could serve as a precursor to catastrophic failures which result in grave losses [1]. A lot of technological efforts have been put into developing strategies of mitigating corrosion through materials selection, changes in design philosophies and the adoption of varied prevention techniques. The use of inhibitors has been well documented as an effective method of protecting metallic materials from corrosion [2]. Many industrial processes have put to use inorganic inhibitors for corrosion protection but as a result of cost and toxicity, attention is currently shifted towards the use of more eco-friendly inhibitors [3-4]. Organic substances *(plant based)* containing functional groups with oxygen, nitrogen and /or sulphur atoms in a conjugate system have been reported to exhibit good inhibiting properties [4-7]. This has made plant extracts an important choice for environmentally friendly, readily available and renewable source for wide range of inhibitors referred to as green inhibitors [5]. Some of the advantages of green inhibitors are low cost of processing, biodegradability, and absence of heavy metals or other toxic compounds which pose great hazard to the environment [8]. A number of successful studies on the use of plant extract as corrosion inhibitors have been investigated and reported by several authors [9-16]. There are however concerns on the sustainability of the use of some of these green inhibitors when commercial scale processing is of interest, since some of the extracts can only be derived from specific plants which are still utilized for so many other applications; coupled with the fact that some of these plants are seasonal. These factors place limits to the extent most green inhibitors could be applied commercially. Lignin however will be an exception – it is a complex chemical compound most commonly derived from wood and an integral part of secondary cell walls of all plants [17]. Since Lignin is an integral part of all plants, it does not have the disadvantage of seasonal or location specific availability, which is common to organic inhibitors specific to certain plants. Lignin and its derivatives have been utilized in many applications such as resin synthesis [18], dispersants, emulsifiers, adhesives and ion exchangers [19]. But little attention has been given to its potential corrosion inhibitive properties. Its consideration as a potential inhibitor is informed by its IR spectrum which shows that it contains functional groups such as OH^- which is known to have inhibitive properties. This work will investigate the corrosion inhibition and adsorption characteristics of lignin extract derived from sunflower on medium carbon low alloy steel immersed in H_2SO_4 solution.

Material and Method

Materials Preparation

Medium carbon low alloy steel was utilized as test material for this research. The chemical composition of the steel was determined using a spark spectrometric analyzer; and the composition is as presented in Table 1. The medium carbon steel was cut to dimensions of 20mm length × 10mm diameter for use as test coupons. Surface preparation of the coupons was performed following standard procedures.

Table 1. Chemical composition of the Medium Carbon Low Alloy Steel

Elements	C	Si	S	P	Mn	Ni	Cr	Mo	V	Cu	W	Fe
Wt %	0.337	0.163	0.0464	0.053	0.813	0.102	0.178	0.018	0.0046	0.36	0.0021	balance

Extraction of Lignin

Sun flower which is readily available in the Akure Metropolis was utilized as the source of Lignin. The stems of the plant were cut into small pieces and sun dried. The dried samples were then pulverized into powder using a grinding machine, and sieved using 850µm mesh screen sieve. 150g of the 850µm mesh screen sieved biomass was weighed and added to 1500ml of prepared 15% NaOH solution in a plastic container.

Figure 1. *Lignin extract derived from the processing of the sunflower*

The mixture was immersed in a water bath set at 80^{o}C for 2 hours and stirring of the mixture performed at intervals. The mixture was then removed from the bath and allowed to cool overnight; after which it was filtered and the pH of the filtrate (black liquor) adjusted to 2 by using 40% H_2SO_4. The precipitate formed (Lignin) was filtered and dried in an oven at 60^{o}C. Figure 1 shows representative samples of the Lignin obtained.

Immersion Test

The polished and pre-weighed medium carbon low alloy steel coupons were immersed in 100ml of 1M H_2SO_4 solutions of the respective inhibitor/blank solutions maintained at 303, 313, 323, and 333K in a thermostated bath for 6 hours. After which the coupons were removed washed, cleaned and weighed. Another set of experiment was carried out at room temperature for various concentration of lignin in 1M H_2SO_4 for 12 days. The coupons immersed in these solutions were weighed at two day intervals. Mass loss and corrosion rate measurements were utilized to evaluate the corrosion behaviour of the test samples. The inhibition efficiency (%) was calculated using the relationship: I.E. = $100 \cdot (1 - C.R_{inh}/C.R_{blank})$, where $C.R_{inh}$ and $C.R_{blank}$ correspond to the corrosion rates in the presence and absence of inhibitor respectively.

Characterization and Adsorption Studies

Characterization of the extracted lignin was carried out by FT-IR studies. FT-IR (FTIR-8400S) spectroscopy was employed to determine the type of functional groups present in the lignin responsible for its inhibitive properties.

Results and Discussion

Mass Loss Method

Figure 2 and 3 presents the mass loss and corrosion rate plots for the medium carbon low alloy steel samples immersed in 1M H_2SO_4 with varied concentrations of the lignin extract. It is observed that there is a significant reduction in the mass loss of the steel samples with the addition of the lignin extract in comparison with the sample in which no lignin was added. This clearly indicates that corrosion inhibition of medium carbon low alloy steel immersed in H_2SO_4 solution is improved with the addition of lignin. Furthermore, it is observed that an increase in the concentration of the lignin extract (from between 5g/L -

15g/L) resulted in a moderate decrease in mass loss (from 0.226g/cm^2 for 5g/L to 0.183g/cm^2 for 15g/L).

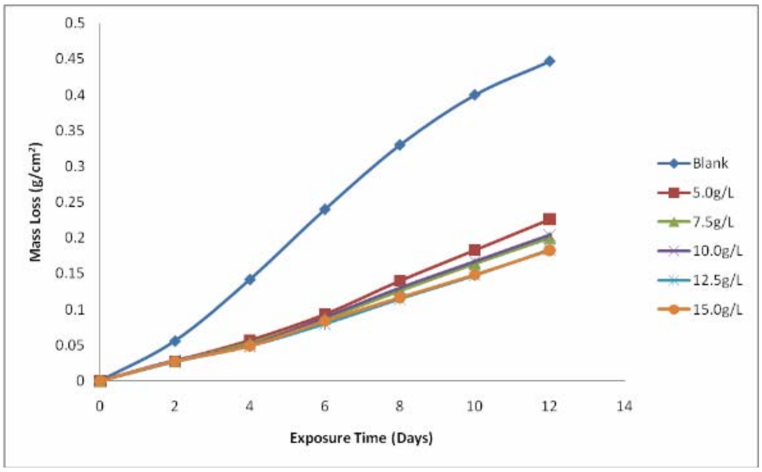

***Figure 2**. Variation of Mass loss with varied concentrations of Lignin in 1M H_2SO_4 Solution*

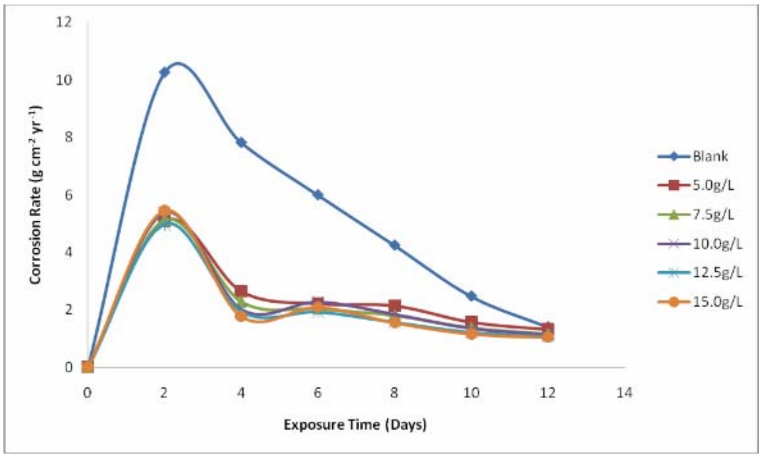

***Figure 3.** Variation of Corrosion rate with varied concentrations of Lignin in 1M H_2SO_4 Solution*

This is an indication that the mass loss is sensitive to the concentration of the lignin extract. This trend is most likely due to the fact that adsorption and surface coverage of the steel increases with concentration of the inhibitor [10]. Thus the surface of the steel is more effectively separated from the medium [20]. The inhibitive effect of the lignin extract is attributed to the presence of some functional groups in the extract as revealed by the Infrared Spectrophotometer result (Figure 4).

It is observed that the extract has OH^- among others which have been reported to contribute to inhibition. The structure of the lignin extract as presented in Figure 5 contains oxygen atom and aromatic rings which are known to serve as centers of adsorption [10].

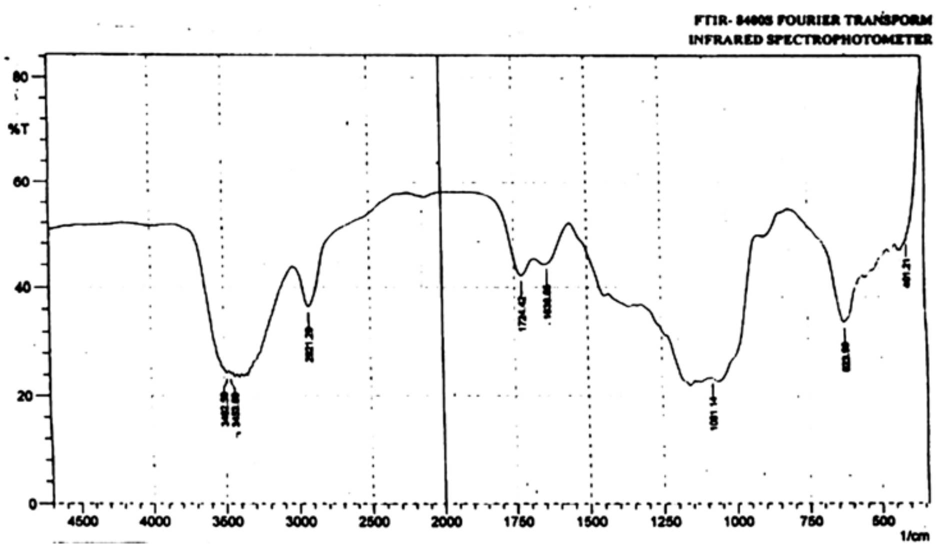

Figure 4. *IR spectrum of Lignin extract of Sunflower*

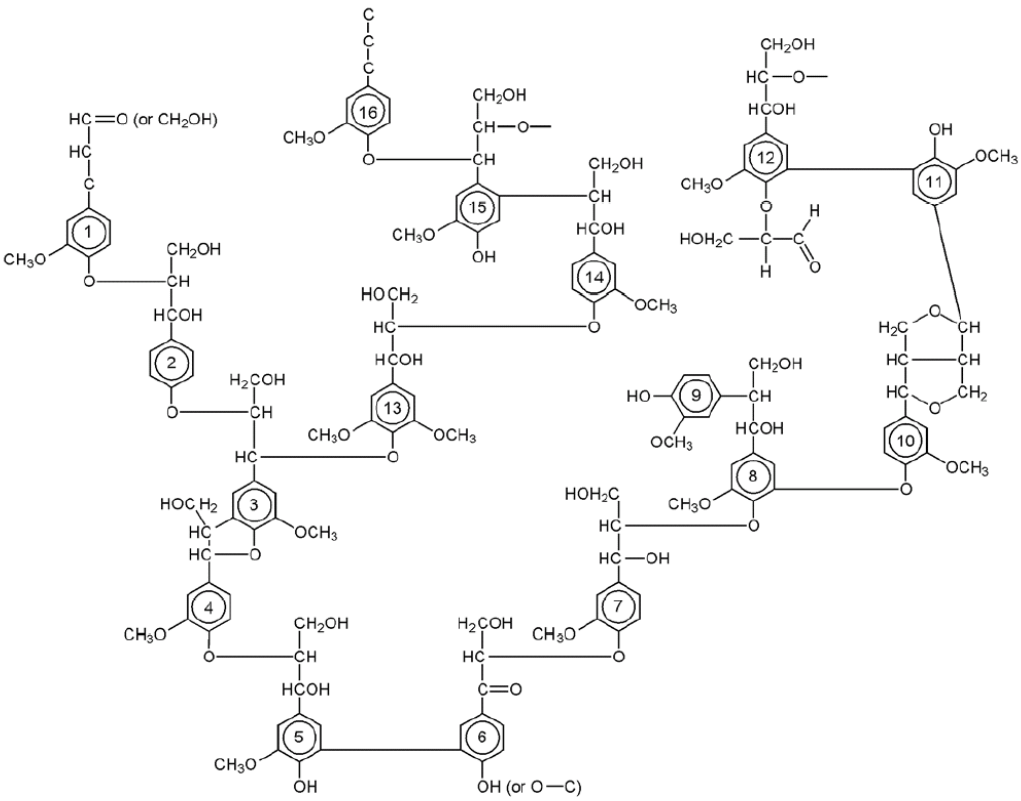

Figure 5. *Structure of Lignin*

The observed trends are well supported by the corrosion rate plots (Figure 3) which show that the corrosion rate reduces sharply after the 4th day of immersion for the samples containing the lignin extract and a gradually reducing rate of corrosion is maintained with further exposure time. This suggests that the adsorption of the lignin was stable for the entire exposure period.

The Effect of Temperature

The stability and mechanism of adsorption of the extract (lignin) on the medium carbon low alloy steel surface was studied by evaluating the variation of corrosion rate and inhibition efficiency with temperature (303K-333K) (Figures 6-7). It is observed from figure 6 that at any of the temperatures, corrosion rate decreases with increase in lignin extract concentration while the corrosion rates increases with increase in temperature. This trend is consistent with the observations of Okafor et al. [21] who reported that the tendency for partial desorption of the inhibitor from the metal surface and the metal dissolution increases with temperature. The variation in inhibition efficiency (Figure 7) did not follow a consistent trend like in the case of the corrosion rates. However, inhibition efficiency of the lignin extract ranged between 55.5% - 78.8% for different temperatures.

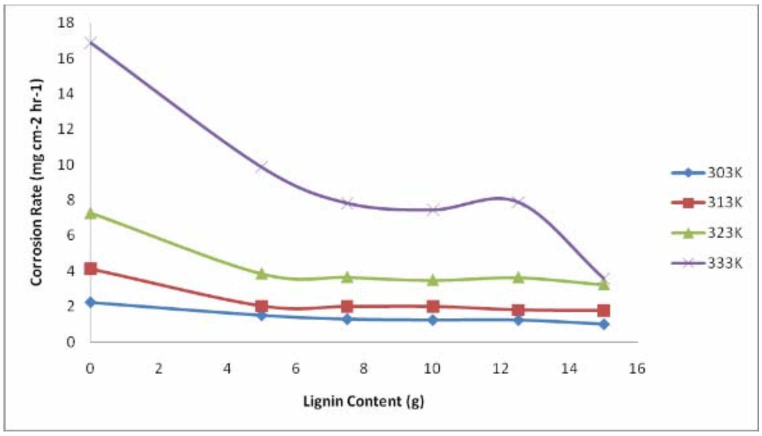

***Figure 6**. Variation of Corrosion rate with temperature*

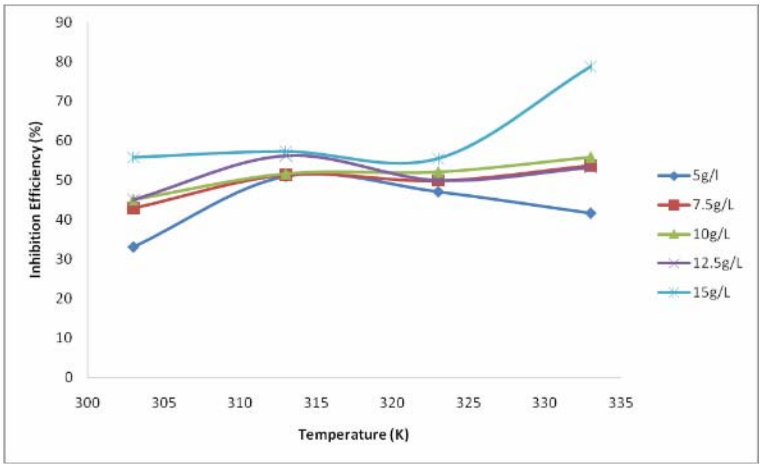

***Figure 7**. Variation of Inhibition Efficiency with temperature for different Lignin Concentration*

Kinetic/Thermodynamics and Adsorption Studies

The adsorption mechanism of organic inhibitors on metal surfaces can be by physical adsorption and chemical adsorption; and is influenced by factors such as nature of the charge of the metal, the chemical structure of the inhibitor, pH, the type of electrolyte and temperature [22]. Thus in order to predict the inhibition mechanism, the activation energy for the corrosion reaction in the absence and presence of various concentrations of lignin at temperatures ranging between 303K-333K was evaluated using the relationship:

$$\text{Log(CR)} = \text{Log(A)} - E_a/(2.303 \cdot R \cdot T)$$

where CR is the corrosion rate, Ea is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. The activation energies were obtained from the slope of the Log CR Vs. 1/T plots for the medium carbon low alloy steel in the absence and presence of lignin as presented in Figure 8.

The estimated activation energies (E_a) from the plots are presented in Table 2. It is observed that the E_a values ranged from 37.46 KJ/mol to 55.6 KJ/mol for all concentrations of lignin. Ebenso et al. [8] reported that values of E_a < 80KJ is indicative of physical adsorption while E_a > 80KJ is indicative of chemical adsorption. Thus the activation energy values support the fact that the lignin extract was physically adsorbed on the medium carbon low alloy steel surface.

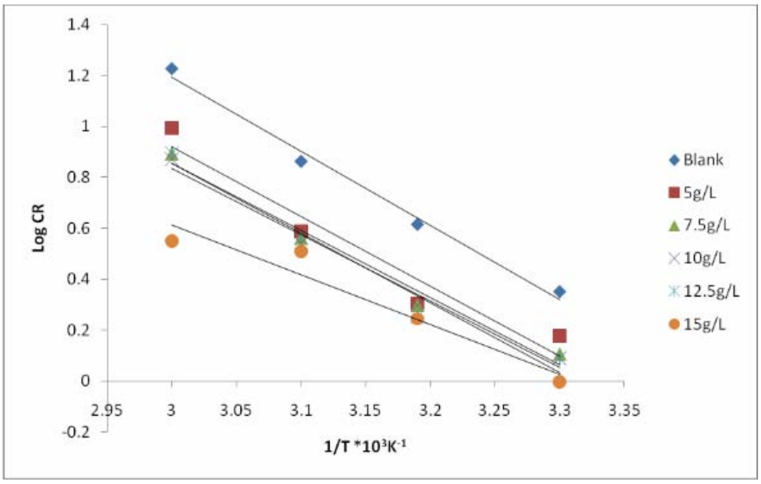

***Figure 8**. Arrhenius plot for medium carbon low alloy steel corrosion in 1 M H_2SO_4 in the absence and presence of lignin extract*

The free energy of adsorption values ΔG^o_{ads}, were obtained from the relationship:

$$\Delta G^\circ_{ads} = -R \cdot T \cdot \ln(55.5 \cdot K)$$

Table 2. Thermodynamics and activation parameters for mild steel in presence of lignin extract in 1 M H_2SO_4

Acid medium	Inhibitor Conc.(g/l)	Ea kJ/mol	-ΔG(kJ/mol) 303K	313K	323K	333K	-ΔS kJ/mol	+ΔH kJ/mol
1 M H_2SO_4	Blank	55.60	-	-	-	-	-	-
	5.0	52.53	13.80	30.02	26.49	21.91	0.20792	43.06
	7.5	50.54	13.98	20.60	19.71	23.70	0.28267	70.39
	10.0	49.95	11.48	15.45	16.22	19.47	0.24735	63.00
	12.5	52.44	9.185	14.89	11.96	14.02	0.11583	24.32
	15.0	37.46	11.78	12.91	12.42	38.21	0.78849	231.91

The values obtained are presented in Table 2. It is observed that the values of the $\Delta G°_{ads}$ are negative in all cases, indicating that the lignin extract is strongly adsorbed on the mild steel surface [23]. Generally, values of $\Delta G°_{ads}$ up to -20kJ/mol are consistent with electrostatic interaction between charged molecules and a charged metal (which indicates physisorption) while those more negative than -40kJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (which indicates chemisorptions) [24].

To further elucidate the mechanism of corrosion adsorption, the adsorption isotherms which provides information on the variation of adsorption with the concentration of the adsorbent (lignin extract in this case) in bulk solution at constant temperature was plotted (Figure 9). The adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions [25]. The experimental data obtained were best fitted with the Langmuir adsorption isotherm which is described by the equation:

$$C/\theta = 1/K_{ads} + C,$$

where (C/θ) is the ratio of inhibitor concentration to surface coverage, K_{ads} the adsorption equilibrium constant.

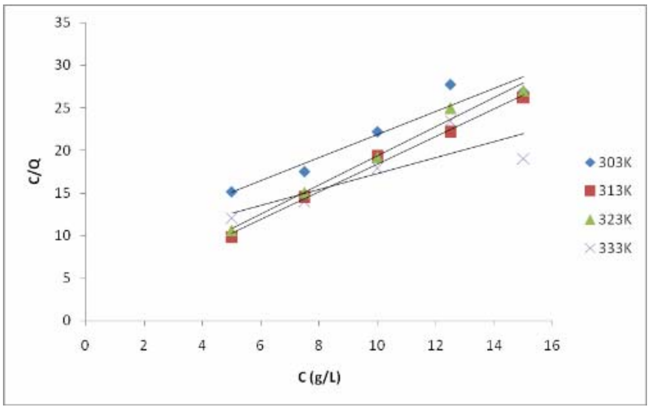

Figure 9. *Langmuir isotherm for the adsorption of lignin on the surface of the medium carbon low alloy steel*

The slopes obtained from the plots were observed to be close to unity; and the isotherm was observed to be best fitted at 313K and 323K where the correlation coefficients were greater than 0.995. This suggests that the adsorption of lignin on the steel is a monolayer adsorption and that there is no interaction between lignin and the medium carbon low alloy steel [26].

Conclusions

From the results obtained from this research investigation, the following conclusions can be drawn:

÷ Lignin extract from sun flower was found to be an efficient inhibitor for the corrosion of medium carbon low alloy steel in 1M H_2SO_4.

÷ The corrosion rates were observed to decrease with increase in concentration of lignin extract but increase with temperature.

÷ The activation energies and the negative free energy of adsorption obtained indicate that the lignin extract is physically adsorbed on the surface of the steel and that the adsorption is strong and spontaneous.

÷ The lignin extract was proved to be an effective eco friendly and low cost inhibitor.

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