Evaluation of Inhibitive Performance of Acidic Extract of *Eichornia Crassipes* on Corrosion of Low Carbon Steel in 1M Sulphuric Acid Solution

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**Abstract** - Corrosion inhibition potential of *Eichornia crassipes* extract on low carbon steel in 1M sulphuric acid solution was investigated using gravimetric method and corrosion rate. The experiment was carried out for 3 hours at different concentration of *Eichornia crassipes* extract and temperatures of 26.6°C, 40°C and 60°C. Arrhenius and improved Arrhenius equations were used to determine the thermodynamics properties of the reaction while the nature of the reaction was proposed by adsorption isotherms. The results showed that corrosion rate decreased in the presence of the extract except in 60°C. Inhibition efficiency also increased with extract concentration with the highest (82%) occurring at room temperature and 5% concentration. Inhibition efficiency decreased with increase in temperature with almost no inhibition at 60°C, this is associated with physisorption. Activation energy (Ea) and activation enthalpy (ΔHads) both had positive values and they increased in the presence of *Eichornia crassipes* extract, those for inhibited solution were higher than those for uninhibited solution, these can also be attributed to physisorption. Inhibition reaction obeyed Langmuir adsorption isotherm. Gibbs free energy (ΔGads) calculated for the reaction is -8.509 to -11.767 kJ mol⁻¹.

**Keywords** - Inhibitive performance, acidic extract, *Eichornia crassipes*, low carbon steel, sulphuric acid

1. **Introduction**

Degradation of metals is a common sight around us. This is known as corrosion and its effects are not desirable because qualities of engineering materials are jeopardized. Acids such as sulphuric and hydrochloric are often used for cleaning metals in the oil and chemical industries but they often leave behind corrosion of the metals. Continuous efforts are on-going towards reducing, if possible, completely eliminating corrosion. Inhibitors are employed for this purpose as they possess substances capable of reducing the reaction between a metal and its environment (Rani and Basu, 2012). Inhibitors can be organic or inorganic depending on their sources. The organic inhibitors can be synthetic or natural. Organic inhibitors have been established to be the best as they are biodegradable, nontoxic and environmentally friendly (Naik et al., 2016).

Organic compounds contain functional groups in their molecular structures that contain O, N, S, P atoms and multiple bonds that inhibit corrosion by displacing the water molecules on the metal and forming barrier against corrosion (Rani and Basu, 2012; Naik et al., 2016). Organic compounds can be expensive sometimes putting limitations to their applications. Attention is being given to natural plants as they are cheap, highly available, nontoxic, and environmentally friendly (Khadraoui et al., 2015). Plants possessing some of the atoms mentioned above have been and are still being investigated for their corrosion inhibition potentials. Plants are rich source of free radical scavenging molecules such as vitamins, terpenoids, phenolic acids, lignins, stilbenes, tannins, flavonoids, quinones, coumarins, alkaloids, amines, betalains and other metabolites which are rich in antioxidant activity (Lalitha and Jayanthi, 2012).

El-Etre (2006) carried out corrosion inhibition of natural honey on copper and reported that it was a good inhibitor. Opuntia extract, aloe vera leaves, orange and mango peels were evaluated by Saleh, Ismail and El Hosary (1982) to be good corrosion inhibitors to steel in 5 and 10% hydrochloric acid solution at temperatures of 25 and 40°C. Srivatsava and Srivatsava (1981) worked on tobacco, black pepper, castor oil seeds, acacia gum and lignin and concluded that they made very good inhibitors for steel in acid medium.

Ethanolic extract of *Ricinus communis* leaves was studied for the corrosion inhibition of mild steel in acid media by Anauda et al. (2005). *Telferia occidentalis* extract inhibited corrosion in both sulphuric and hydrochloric acid media (Oguzie, 2004). *Stevia rebaudiana* leaves extract according to Cang, Shao and Xu (2012) inhibited mild steel corrosion in sulphuric acid solution. The inhibition which was said to occur via adsorption on the metal surface was reported to increase with extract concentration. Aquatic plants are incredibly rich in naturally occurring chemical compounds (organic acids, glucosinolates, alkaloids, flavonoids, terpenoids, polyphenols, and tannins) and most of them are known to have corrosion inhibition efficiency (Manimegalai and Manjula, 2015). Shanab and Shalaby (2012) investigated the corrosion inhibition potential of crude methanolic extract of Water hyacinth (*Eichornia crassipes*) on magnesium alloy (AZ31E) in 0.15M NaCl and concluded that though initially the rate of inhibition was low but it later increased with extract concentration. Ulaeto et al. (2012) applied the acid extract of the roots and leaves of *Eichornia crassipes* to inhibit mild steel corrosion in hydrochloric acid using gasometric technique and reported that inhibition took place through physisorption.

Corrosion inhibition performance of plant extracts depends on the part of the plant and its location. One
compound effective in a certain medium with a given metal may be ineffective for the same metal in another medium (Okafor et al., 2005). They investigated corrosion inhibition potential of acidic extract of *Eichhornia crassipes* on low carbon steel in 1M sulphuric acid. This may contribute to reduction of the cost of corrosion prevention in the industry as *Eichhornia crassipes* is highly available and posing environmental menace. *Eichhornia crassipes* can be found almost everywhere in the tropics and subtropics. It grows in ponds, pools, water tanks, lakes, even in irrigation channels. A plant that was initially prized for its beautiful flowers and was propagated as an ornamental plant by botanical gardens that later became one of the worst ecological problems in the world especially in Africa due to its aggression. Shorelines are literally choking from the ecological effect of Water hyacinth which has lead to the plant being infamous worldwide (Teygeler, 2000). *Eichhornia crassipes* is a free-floating perennial aquatic herb. However, phytochemical studies carried out revealed the presence of nutritionally important compounds like phenolics, flavonoids, glutathione and many other metabolites (Lalitha and Jayanthi, 2012). Some of these phytochemicals have been responsible for antioxidant activity in green inhibitors.

2. EXPERIMENTAL METHODS

2.1 Specimen Preparation

Low carbon steel sheet was mechanically cut into dimensions 2 cm x 2 cm x 0.1 cm. A hole of 0.1 cm diameter was drilled in each of the specimens through which a string was passed for ease of suspension. The surfaces of the specimens were polished mechanically, cleansed in acetone and rinsed in distilled water prior to their use for the corrosion studies.

2.2 *Eichhornia crassipes* Extract Preparation

Fresh plants of *Eichhornia crassipes* used for this work were obtained from the lagoon side of University of Lagos, Akoka, Nigeria, though it is equally possible to collect them from ponds, channels and water tanks. They were cleaned and dried in a shade until there was no variation in weight. The dried leaves were pulverized and the extract was obtained by soaking 10g of the pulverized plant in 100 ml of 1M H2SO4 acid for 48 hours (Cang, Shao and Xu, 2012; Patel et al., 2013; Ibis, Ngwamaghi and Okoroafor, 2015), after which it was filtered and the extract was mixed with 1M H2SO4 acid at concentration of 1%, 3% and 5% (v/v) for corrosion studies.

2.3 Gravimetric Studies

Gravimetric analysis was carried out by immersing the specimens into 50ml solution of 1 M H2SO4 acid in the absence and presence of the extract for the period of 3 hours. The experiment was carried out at 3 different temperatures (room temperature (26.6°C), 40°C and, 60°C and in triplicates. The weight of the specimens before and after immersion was determined using analytical weighing balance. The weight loss (ΔM) was calculated from the difference between initial (Mi) and final (Mf) weights. The average weight loss for three identical experiments was obtained and the Corrosion Rate (CR) is expressed according to Oguzie et al. (2008) and AbdEl Haleem et al. (2013) in Eq. 1

\[
CR = \frac{\Delta W}{ST}
\]

where, CR= corrosion rate
\(\Delta M=\) weight loss
S = surface area of specimen
T= time in hours

Inhibition Efficiency (IE%) of the extract was determined according to Abd El Haleem et al. (2013) in Eq. (2)

\[
IE\% = \left(1 - \frac{CR_{o}}{CR_{blank}}\right) \times 100
\]

where, \(CR_{o}=\) Corrosion rate with inhibitor
\(CR_{blank}=\) Corrosion rate without inhibitor

3. RESULTS AND DISCUSSION

3.1 Chemical composition of steel sample

Results of the chemical analysis of the steel sheet revealed the chemical composition as: (wt%) Fe (98.4%), C (0.08%), Si (0.072%), Mn (0.498%), Ni (0.06%), Cr (0.0089%), Cu (0.53%), Co (0.183%), Al (0.015%), Mg (0.049%) S (0.062%), P (0.013%) with trace of other metals making up the balance.

3.2 Weight loss, corrosion rates and inhibition efficiency

Figures 1 and 2 show the weight loss and corrosion rates curves at all concentrations for the inhibition performance being investigated. It can be observed that weight loss and corrosion rate generally decreased in the presence of *Eichhornia crassipes* extract. This makes the plant a good corrosion inhibitor. The inhibition efficiency and surface coverage of the investigation are as shown in Table 1. Surface coverage is directly proportional to inhibition efficiency for any corrosion inhibition process. Inhibition generally increased in the presence of the extract (except in the case of 60°C) and more extract concentration led to more inhibition with the highest (82%) occurring at room temperature in 5% extract concentration. The protection barrier offered by the extract reduced at 60°C. This in addition to aggressive corrosion associated with low carbon steel in high temperature led to reduced inhibition efficiency.

![Fig. 1: Plot of Weight Loss against Concentration for all Absolute Temperatures](image-url)
3.2 Effect of Temperature on Performance

Metals are sometimes subjected to operations at higher temperatures than the room temperature. This makes corrosion inhibition at high temperature very important, hence the reason for carrying out weight loss experiment at temperatures of 26.6°C (room temperature), 40°C and 60°C. The results obtained were used to calculate the thermodynamics parameters for the study. The relationship between the corrosion rate of a metal in corroding media can be obtained using Arrhenius Equation given by Eq. 3 according to Alane and Oluosegan (2012).

\[
\ln(CR) = \ln A - \frac{E_a}{2.303RT}
\]  

(3)

The activation entropy and activation enthalpy for the study were calculated using improved Arrhenius equation given by Eq. 4 according to Khadom et al. (2009).

\[
CR = \frac{RT}{Nh} \exp \left( \frac{\Delta S_{act}}{R} \right) \exp \left( -\frac{\Delta H_{act}}{RT} \right)
\]  

(4)

where, \(E_a\) is the apparent activation energy, \(R\) is the molar gas constant, \(T\) is the absolute temperature and \(A\) is the frequency factor, \(\Delta S_{act}\) is the activation entropy, \(\Delta H_{act}\) is the activation enthalpy, \(N\) is Avogadro’s number and \(h\) is Planck’s constant.

The slopes of Arrhenius plot of \(\ln(CR)\) against the reciprocal of absolute temperature (1/T) for the corrosion of low carbon steel in 1M sulphuric acid solution in the absence and presence of Eichhornia crassipes extract gave the \(E_a\) for the system under investigation. The thermodynamics parameters for this study are shown in Table 2. It can be seen from this table that the values of \(E_a\) which represent the total values of energy of activation including the energy required for the removal of corrosive media molecules (Laitha and Jayanthi, 2012), increased in the presence of the extract with its absence and \(E_a\) increased with increase in extract concentration. This means that the activation energy for the system was increased by the extract. This agrees with the reports of Obi-Egbedi, Obot and Umoren (2012), Ulaeto et al. (2012), Al-Haj-Ali et al. (2014) and Naik et al. (2016) for physisorption inhibition where the \(E_a\) values for the inhibited were greater than the uninhibited. Labrabi et al. (2005) and Khadraoui et al. (2015) also attributed higher activation energy in the presence of inhibitor compared with its absence to physisorption inhibition, while the reverse was associated with chemisorption. Also, the slopes and the intercepts of improved Arrhenius plot of \(\ln(CR/T)\) against 1/T gave the \(\Delta H_{act}\) and \(\Delta S_{act}\) respectively for the system. These values of \(\Delta S_{act}\) and \(\Delta H_{act}\) are also shown in Table 2 where it can be seen that \(\Delta S_{act}\) has negative values depicting greater order during activation process. It can be observed from Table 2 that \(\Delta H_{act}\) increased in the presence of the Eichhornia crassipes with its largest value occurring at 5% concentration. In a nutshell, \(E_a\) and \(\Delta H_{act}\) increased with inhibitor concentration, this trend of \(\Delta H_{act}\) agrees with what was reported for physisorption (Fouda, Al-Sarawy and El-Kator, 2006; Alane and Oluosegan, 2012; Al-Mhyawi, 2014). The positive values of \(\Delta H_{act}\) reflect endothermic nature of the reaction in the presence of the extract.

### Table 1. Inhibition efficiency and surface coverage for the corrosion of low carbon steel in 1M sulphuric acid in the presence of Eichhornia crassipes extract

| Concentration | Inhibition Efficiency (%) | Surface Coverage, \(\theta\) (IE/100) | Absolute Temperatures |
|---------------|---------------------------|-------------------------------------|----------------------|
|               |                           |                                     | 26.6°C | 40°C | 60°C | 26.6°C | 40°C | 60°C |
| Blank         |                           |                                     | 0.015  | 0.025 | 0.035 | 0.025  | 0.035 | 0.03  |
| 1% (v/v)      |                           |                                     | 0.37   | 0.30  | 0.38  | 0.33   | 0.35  | 0.32  |
| 3% (v/v)      |                           |                                     | 0.71   | 0.72  | 0.74  | 0.72   | 0.79  | 0.77  |
| 5% (v/v)      |                           |                                     | 0.82   | 0.81  | 0.84  | 0.81   | 0.82  | 0.84  |

### Table 2. Thermodynamic and activation parameters for corrosion of low carbon steel in 1 M sulphuric acid solution in the presence of Eichhornia crassipes extract

| Concentration | \(E_a\) (kJ mol\(^{-1}\)) | \(\Delta H_{act}\) (kJ mol\(^{-1}\)) | \(\Delta S_{act}\) (J mol\(^{-1}\)K\(^{-1}\)) |
|---------------|-----------------------------|-------------------------------------|-----------------------------------------------|
| Blank         | 1.6                         | -1.93                              | -281.445                                      |
| 1% (v/v)      | 3.33                        | -1.19                              | -282.61                                       |
| 3% (v/v)      | 20.77                       | 6.40                               | -264.36                                       |
| 5% (v/v)      | 55.96                       | 21.67                              | -215.76                                       |

3.3 Adsorption Parameters Considerations

The mechanism of inhibition can be understood by studying the adsorption isotherms which provide further information on the variation of adsorption with the concentration of extracts at constant temperature (Alane and Oluosegan, 2012). It is assumed that inhibitors prevent corrosion reaction through the blockage of active sites on the metal surface by adsorbed species of extract. It then means that corrosion will only occur in the area where there is no coverage. Inhibition efficiency is directly proportional to surface coverage (Khadom et al., 2009). The experimental data fitted into Langmuir isotherm model given according to Obi-Egbedi, Obot and Umoren (2012) by Eq.5.

\[
\frac{C}{\theta} = \frac{1}{K_{ads}} + C
\]  

(5)

where, \(\theta\) = surface coverage (fraction, dimensionless).
C = extract concentration and $K_{ads}$ = adsorptive equilibrium constant
Plot of $C/\theta$ against $C$ showing the correlation coefficients (R2) is given by Figure 3.

The standard free energy of adsorption $\Delta G_{ads}^\circ$ was calculated using Eq. 6 in accordance to Zhang et al. (2010) and Al-Mhyawi (2014).

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}^\circ}{RT}\right)$$

where, 55.5 is the concentration of water in the solution in 1 mol-dm$^{-3}$, R the universal gas constant and T the thermodynamic temperature. Table 4 gives the adsorption parameters.

The negative values of $\Delta G_{ads}^\circ$ depicts the spontaneity of the adsorption process and the stability of the adsorbed species on the low carbon steel surface (Khadom et al., 2009; Shukla and Ebenso, 2011). Generally, $\Delta G_{ads}^\circ$ of -20 kJ mol$^{-1}$ or lower are said to be consistent with the electrostatic interaction between charged organic molecules and the charged metal surface indicating physisorption (Abd El Haleem et al., 2013; Obi-Egbedi, Obot and Umoren, 2012). The $\Delta G_{ads}^\circ$ for this system is from -8.509 and -11.767 kJ mol$^{-1}$ which indicates physisorption.

![Fig. 3: Langmuir Isotherm for adsorption of *Eichhornia crassipes* extract](image)

### Table 3. Adsorption parameters for corrosion of low carbon steel in 1 M sulphuric in the presence of *Eichhornia crassipes* extract

| Temperature | $R^2$ | $K_{ads}$ (mol$^{-1}$) | $\Delta G_{ads}^\circ$ (kJ mol$^{-1}$) |
|-------------|-------|-----------------------|--------------------------------------|
| 299.6 K     | 0.997 | 0.5486                | -8.509                               |
| 313 K       | 0.904 | 0.7936                | -9.850                               |
| 333 K       | 0.957 | 1.2639                | -11.767                              |

### 4. CONCLUSION

The inhibition potential of *Eichhornia crassipes* extract on low carbon steel in 1 M sulphuric acid at different temperatures using gravimetric method was investigated in this study. Results obtained showed that *Eichhornia crassipes* was a good corrosion inhibitor of low carbon steel in 1 M sulphuric acid environment and its performance increased with extract concentration but decreased with temperature. It can be concluded that *Eichhornia crassipes* can be put to industrial use in corrosion prevention due to its high availability thereby reducing its environmental stigma.

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