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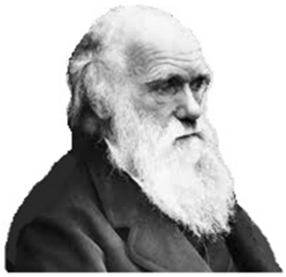

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Retarding Carbon Steel Dissolution in Oil Well Acidizing Solution using Leave Extracts of *Evolvulus alsinoides* (Linn.) Linn. [Family: Convolvulaceae]

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ABSTRACT

The corrosion inhibition performances of leave extracts of *Evolvulus alsinoideson* (EA) X70 carbon steel in 5% HCl was investigated using weight loss and surface analysis. Weight loss measurement showed that this leave extract has high inhibiting properties for X70 steel corrosion in acidic solution and the inhibition efficiency increased with the increase in inhibitor concentration. The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the X70 steel surface. Adsorption of EA on the X70 steel surface in 5% HCl obeys the Langmuir adsorption isotherm. Gibbs free energy of adsorption was calculated and indicated that adsorption occurred through physical and spontaneous process. Scanning electron microscopy (SEM) of the inhibitor-adsorbed steel surface affirmed the adsorption of inhibitor and improvement in the surface smoothness of the X70steel.

***Keywords*:** Corrosion inhibition, *Evolvulus alsinoideson*, X70 steel, surface analysis, mixed-type inhibitor, Langmuir adsorption isotherm

1. INTRODUCTION

Steel is used in many industrial applications, such as the oil and gas processing industry, water pipes, refining and extraction, cooling water systems, boilers, and skyscrapers. Acid solutions are widely used in industries for lots of purposes, such as acid descaling, industrial acid cleaning, acid pickling and oil well acidizing [1, 2]. Nowadays, various preventive methods

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are available to reduce the corrosion rate of metals in acidic environment. Among them, the use of inhibitors has been reported to be one of the most operational and functional approaches against corrosion. Organic materials inhibit corrosion by adsorption; hence, inhibitors with the ability to adsorb on the metal surface will hinder the dissolution or corrosion reaction of such metal in the corrosive medium [3, 4]. The significance of this metal protection process in diverse areas of applications has necessitated the keen interest in research in corrosion chemical inhibition by various corrosion scientists among others [5-8].

Although numerous synthetic compounds presented good anticorrosive action, the majority of them are considered toxic to humans and the environment [9]. Hence, study on less-toxic and more environmentally-friendly or 'green' corrosion inhibitors is encouraged [10]. Green corrosion inhibitors are biodegradable and do not contain toxic substances. Plant extracts are rich in compounds like alkaloids, flavonoids, tannins etc., which have the potential to act as corrosion inhibitor. Some investigations have in recent time been made into the corrosion inhibiting effect of some plant extracts on steel dissolution, which have been found to generally exhibit good inhibition efficiencies [11-15].

The present report continues the focus on the broadening applications of plants extracts for metallic corrosion control and reports on the inhibiting effect of *Evolvulus alsinoides* (EA) plant extracts on X70 carbon steel in 5% HCl solution. EA, commonly known as dwarf morning-glory and slender dwarf morning-glory, is flowering plant from the family Convolvulaceae. In traditional medicine, the whole plant is used in the treatment of neurodegenerative diseases such as brain tonic, amnesia and asthma, epilepsy and as a hepatoprotective. The phytochemical analysis has reported the existence of biomolecules such as β-sitosterol, scopolin, scopoletin, umbelliferon, triacontane and betaine. The choice of EA is due to its low cost and easy availability. Weight loss and electrochemical measurements were used for monitoring corrosion while scanning electron microscopy was used for surface morphology examinations.

2. MATERIALS AND METHODS

2. 1. Materials and sample preparation

X70 carbon steel specimens having weight percentage composition as follows; C: 0.23%; Mn: 1.10%; P: 0.03%; S: 0.008%; Ni: 0.35%; Ti: 0.005%; Cu: 0.15%; Nb: 0.012%; Pb: 0.002% and the remainder being Fe were used. The steel sheet with thicknee 0.2 cm was cut into coupons of dimension 3cm x 2cm, grinded and polished with emery papers (600 to 1200) to get flat surface, degreased with acetone, washed with distilled water and dried prior to each use.

The concentration of the corrosive solution used in this work was 5% HCl solution, prepared from the concentrated 37% HCl reagent by dilution using distilled water.

2. 2. Preparation of plant extract

Evolvulus alsinoides leaves were collected from the plant in the Botanical garden of the University of Port Harcourt, Nigeria. The leaves were placed in an oven for drying at a temperature of 70°C for four hours. An aqueous extract of EA was prepared by grinding 10 g of the dried leaves to powder form and digesting in 1 L of 5% HCl solution. The resultant solution was kept for 24 hours, filtered and stored. From the stock solution (10.0 g L^{-1}), the test solutions of EA leaves extracts were prepared at concentrations of 0.5, 1.0, 1.5 and 2.0 g L^{-1}.

2. 3. Weight loss measurement

The weight loss measurements according to standard method reported by some authors [16-18] were carried out in a 250 ml capacity glass beaker. At the end of the tests, each specimen was weighed and the mean value of the weight loss reported. The corrosion rate (*CR*) were calculated from the following equation [19]:

$$CR = \frac{\Delta W}{At} \times 100 \quad (1)$$

where ΔW is weight loss of the carbon steel specimens (mg); *A* is the area of the carbon steel specimen in cm^2 and *t* is the exposure time in *h*. From the corrosion rate, the surface coverage (θ) as a result of adsorption of inhibitor molecules, and inhibition efficiencies of the molecules (η_{WL}%) were determined using equations (2) and (3), respectively.

$$\theta = \frac{CR_{(blank)} - CR_{(inh)}}{CR_{(blank)}} \quad (2)$$

$$\eta_{WL}\,(\%) = \frac{CR_{(blank)} - CR_{(inh)}}{CR_{(blank)}} \times 100 \quad (3)$$

where $CR_{(blank)}$ and $CR_{(inh)}$ are the corrosion rate in the absence and presence of the inhibiting molecules, respectively.

2. 4. Surface analysis

The surface morphology of the X70 carbon steel coupons were studied using Ziess Evo 50 XVP model of SEM. A coupon was immersed in blank 5% HCl while the second coupon was immersed in a solution of 5% HCl with 2.0 g L^{-1} EA in HCl for 8 hours. Further, the specimens were removed, cleaned with deionized water, dried and analyzed by SEM.

3. RESULTS AND DISCUSSION

3. 1. Weight loss measurements

3. 1. 1. Effect of inhibitor concentration

The inhibition efficiencies (η_{WL}) surface coverage (θ) and corrosion rates (C_R) obtained from weight loss measurements at different concentrations of EA in 5% HCl are given in Table 1. Figures 1(a) and 1(b) show the variation of corrosion rate ane inhibition efficiency with inhibitor concentration at different temperatures. From Table 1 and Figure 1, it is found that inhibition efficiency increases and corrosion rate decreases with increasing inhibitor concentration. This behavior can be explained based on strong interaction of the inhibitor molecule with the metal surface resulting in adsorption [20, 21]. The maximum inhibition efficiency (96.6%) for EA extract was obtained at 2.0 g L^{-1} concentration and 30 °C. These results show that EA can act as effective inhibitor for X70 steel corrosion in acid solution in the concentration range studied.

Table 1. Weight loss data for X70 steel in 5% HCl solution in the absence and presence of various concentrations of EA extract at different temperatures

Temp. (K)	EA Conc. ($g\ L^{-1}$)	*CR* ($mg\ cm^{-2}\ h^{-1}$)	η_{WL} %	θ
303	0	5.342	-	-
	0.5	1.965	63.2	0.632
	1.0	1.113	79.2	0.792
	1.5	0.614	88.5	0.885
	2.0	0.179	96.6	0.966
313	0	8.971	-	-
	0.5	3.828	57.3	0.573
	1.0	2.750	69.3	0.693
	1.5	1.992	77.8	0.778
	2.0	1.026	88.6	0.886
323	0	11.164	-	-
	0.5	5.611	49.7	0.497
	1.0	3.916	64.9	0.649
	1.5	2.899	74.0	0.740
	2.0	1.710	84.7	0.847

3. 1. 2. Adsorption isotherm

The most preferable way to study quantitatively the adsorbed layer of organic inhibitor responsible for the restricted access of aggressive species from the corrosive environment to the metal surface is by adsorption isotherm. In our present study, in order to clarify the nature and strength of adsorption, Langmuir, Freundlich, Frumkin and Temkin isotherms were tested. Langmuir adsorption isotherm gave the best fit judging from near unity values of the observed regression coefficient (R^2). The Langmuir isotherm is given by the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (4)$$

where K_{ads} is the equilibrium constant of adsorption/desorption process, θ is surface coverage and C is the inhibitor concentration. Plots of C/θ against C yield straight lines as shown in Figure 2, and the corresponding linear regression parameters are listed in Table 2.

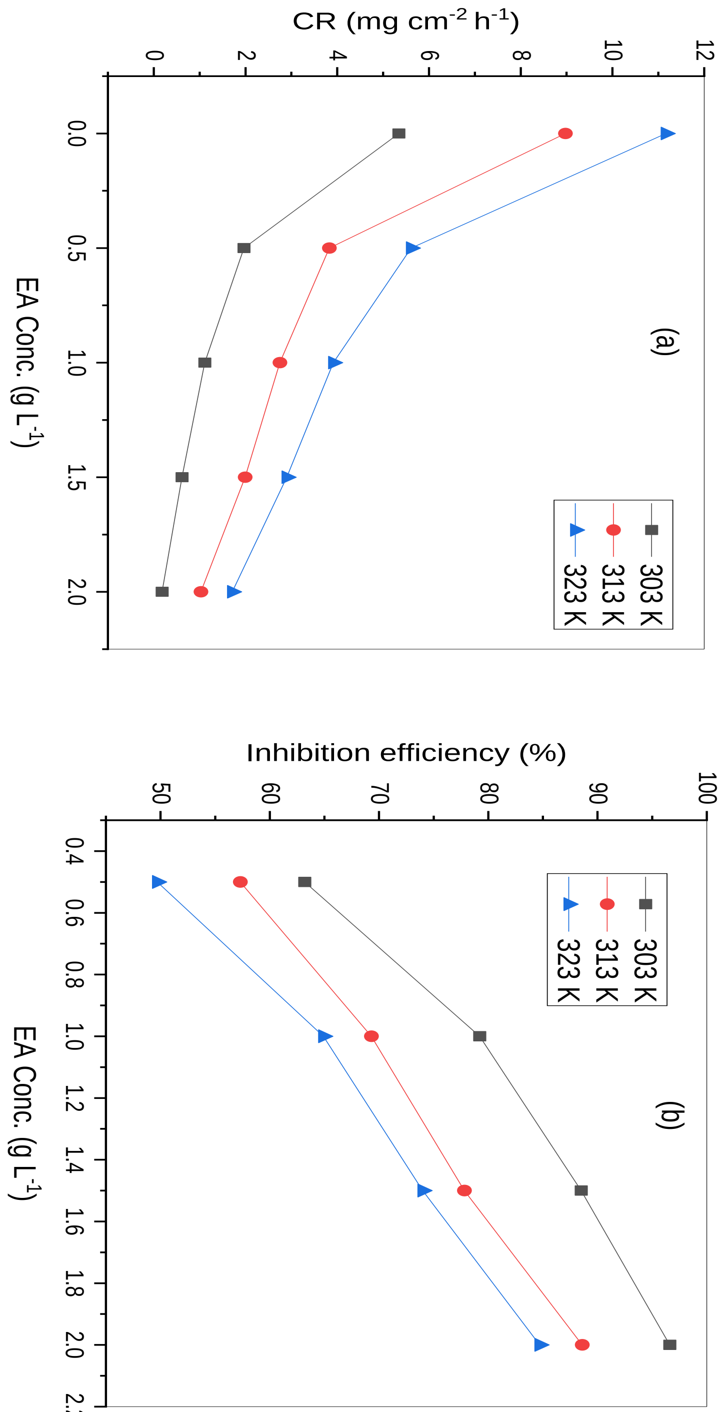

Figure 1. Plot of (a) corrosion rate and (a) inhibition efficiency with EA concentrations for X70 carbon steel in 5% HCl solution at various temperatures

The slopes of the lines were approximately unity (Table 2) with negligible errors, which was in agreement with the theoretical basis of Langmuir isotherm [22]. These parameters indicate that the adsorption of EA inhibitor on X70 steel surface obeys Langmuir adsorption isotherm. This isotherm assumes that the adsorbed molecules occupy only one site and there are no interactions with other adsorbed species [23-32]. The K_{ads} is reported to be related with the standard free energy of the adsorption process. The value of K_{ads} obtained can be used to calculate the standard free energy (ΔG^{o}_{ads}) via the following equation:

$$K_{ads} = \frac{1}{A}\, exp\left(-\frac{\Delta G^{o}_{ads}}{RT}\right) \qquad (5)$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature and A is the density of water (1000 g L^{-1}). The computed values of K_{ads} and ΔG^{o}_{ads} are listed in Table 2. The large K_{ads} value gives better inhibition efficiency due to strong interaction between the metal surface and adsorbing inhibitor molecules while a small K_{ads} value compromise that such interactions between the adsorbing inhibitor molecules and the metal surface are weaker, indicating that the inhibitor molecules are easily removable by the solvent molecules from the surface [25]. The negative value of ΔG^{o}_{ads} indicates that the inhibitor is spontaneously adsorbed onto the X60 steel surface. Values of ΔG^{o}_{ads} are always used to classify adsorption process as physisorption (when ΔG^{o}_{ads}= -20 kJ mol^{-1}, or less negative) or chemisorption (for ΔG^{o}_{ads}= -40 kJ mol^{-1} or more negative). In the present study, the value of ΔG^{o}_{ads} are between -19.79 kJ mol^{-1} and 19.97 kJ mol^{-1} which probably means that the adsorption of EA on the X70 steel surface exhibits physical adsorption.

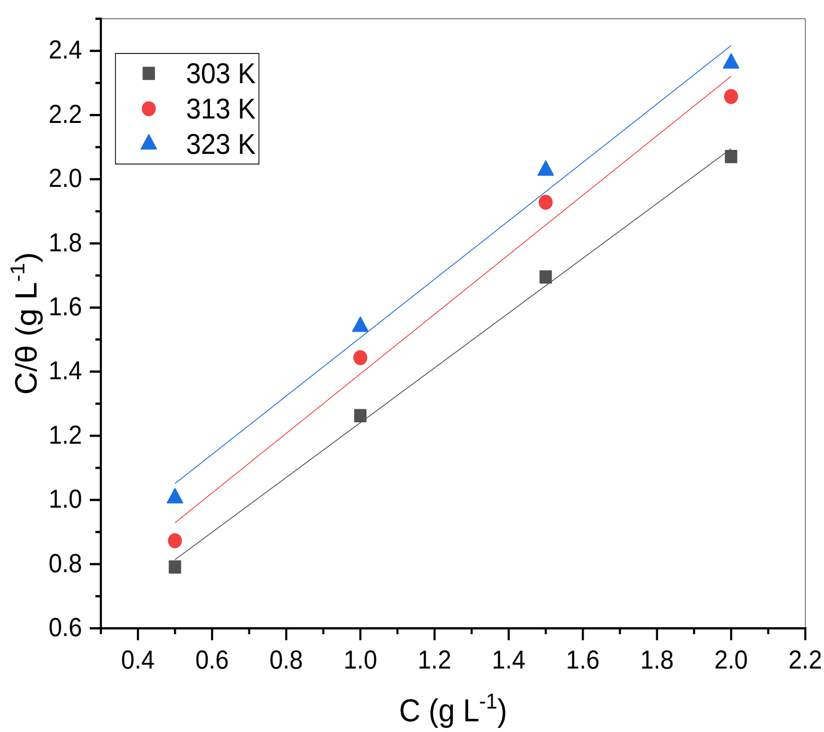

Figure 2. Langmuir isotherm for the adsorption of EA on the X70 steel surface.

Table 2. Adsorption parameters derived from Langmuir adsorption isotherm

Temp. (K)	Slope	R^2	K_{ads}	ΔG^o_{ads} (kJ mol^{-1})
303	0.8540	0.9975	2.5822	-19.79
313	0.9279	0.9865	2.1486	-19.97
323	0.9174	0.9899	1.6784	-19.94

3. 2. Surface analysis

The changes that take place on the surface of the X70 steel specimen were studied in 5% HCl solutions in the absence and in the presence of EA extract after 8 h immersion time and are given in Figure 3a & 3b. The X70 steel specimen in blank 5% HCl without the inhibitor (Figure 3a) was severely corroded with a rough surface due to localized attack of hydrochloric acid thus forms a rust product on the surface. On addition of EA extract, the damage was reduced (Figure 3b), with significantly smooth surface. This signifies that the development of shielding layer by the inhibitor on the metal surface acts as a blockade of corrosion attack by the acid solutions.

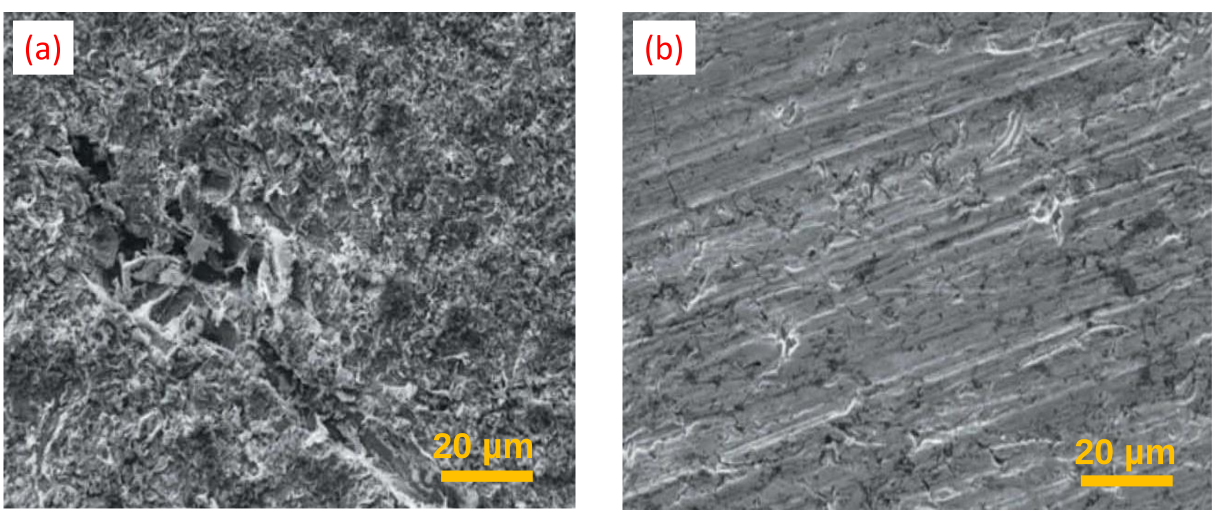

Figure 3. SEM micrographs of **(a)** X70 steel treated with 5% HCl without inhibitor, **(b)** X70 steel treated with 2.0 g L^{-1} EA extract

4. CONCLUSIONS

The corrosion inhibition and adsorption studies of EA extract on X70 steel in 5% HCl solution was examined. The outcome shows the following:

1. The *Evolvulus alsinoides* (EA) plant extracts act as good X70 steel corrosion inhibitor in in 5% HCl. The inhibition efficiency increases and corrosion rate decreases with increase in concentration of EA. The maximum efficiency of 96.6% was achieved for 2.0 g L^{-1} of EA extract.
2. The adsorption of inhibitor molecules on the X70 steel surface obeys Langmuir adsorption isotherm. The negative values of free energy of adsorption (ΔG^{o}_{ads}) indicate that the adsorption process is spontaneous and physically adsorbed on the mild steel surface.
3. The surface morphology studies of the X70 steel substrates by scanning electron microscope also conclude the formation of protective layer.

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