PRINT ISSN 1119-8362
Electronic ISSN 1119-8362

Full-text Available Online at
https://www.ajol.info/index.php/jasem
http://www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage.
Vol. 24 (4) 707-712 April 2020

Corrosion Inhibition Behaviour of *Enantia chlorantha* Extract on Pipeline Steel Corrosion in Acidic System

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ABSTRACT: The corrosion inhibition capacity of *Enantia chlorantha* bark (ECB) extract on the corrosion of pipeline steel in an acidic environment was studied using the gravimetric method. The result revealed that weight loss obviously increased with the rise in temperature though trend lines were not parallel. The results obtained from the evaluation showed that the corrosion inhibition efficiency of the extract increased with extract concentration attaining an efficiency of 89.02% with 2.5 g/L concentration at 30 ºC. The corrosion inhibition efficiency, however, decreased with increase in temperature, while the corrosion rate decreased. The significant achievement in this study was the ability of *Enantia chlorantha* extract to reduce the corrosion rate constant, increase its surface coverage with consequent longer material half-life in an acidic environment.

DOI: https://dx.doi.org/10.4314/jasem.v24i4.24

Dates: Received: 04 February 2020; Revised: 14 March 2020; Accepted: 22 March 2020

Keywords: Inhibition efficiency, surface coverage, plant extract, weight loss, half-life

Materials and systems can only move from equilibrium state to a state of non-equilibrium when acted upon by external force/energy. According the second law of thermodynamics, once in a state of non-equilibrium, there is a natural tendency for the systems/materials to move back to equilibrium state (David and Norman, 1996). Therefore all refined materials corrode. Corrosion can therefore be referred to as thermodynamically inevitable process. The corrosion rate of metals is much higher due to their high electronic potential (Fontana, 1987). The corrosion of metals is of great cost to the industrialist and environmentalist and consequently the national economy (Fontana, 1987). Efforts to mitigate corrosion has been greatly limited because environmental concerns and consequent regulations. Corrosion is mostly controlled by electrical methods and separating the corrodant and the material. Coating and the use of corrosion inhibitors are ways establishing barrier between metals and corrodants (Obot *et al.,* 2012; Shanmugam *et al.,* 2013). However, most synthetic compounds used as corrosion inhibitors are expensive, non-renewable and toxic to the ecosystem. Extracts from natural sources like plants have been published as effective corrosion inhibitors (Obot *et al.,* 2012; Ngobiri *et al.,* 2013; Dharmaraji *et al.,* 2017).

Plant extracts are abundant and easily renewable as well as cheap. Hence, their popularity as good alternative to toxic corrosion inhibitors. The corrosion inhibition of these phyto extracts has been severally attributed to their rich organic constituents which are most times hetro in nature (Ngobiri *et al.,* 2015; Olusegun *et al.,* 2017). Corrosion inhibition mechanism of inhibitors has been severally linked to adsorption of inhibitor molecules on the metal. This organic functionality provides bonding sites for the inhibitor on the metal surface thereby establishing a barrier against the corrodant (Eddy and Ebenso, 2008; Singh and Quraishi, 2017).This paper presents the corrosion inhibition capacity of the extract of the bark of a popular West African herb *Enantia chlorantha Oliv* (Adesokan *et al.,*2008).*Enantia chlorantha Oliv*is commonly called African yellow wood.It belongs to the family of Annonaceae and it is locally known as Awogba, Awopa (Yoruba), Erumeru (Igbo), Osomoluand Eremba-Vbogo (Bini). It is an ornamental tree of up to 30m high, with dense foliage and spreading crown.*Enantia chlorantha* has many therapeutic properties like anti cough, diarrhea, jaundice, urinary tract infection and as a treatment for wounds (Gill and Akinwunmi, 1986; Adjanohoun *et al.,* 1996; Atata *et al.,* 2003; Gbadamosi and Oni, 2004). Researchers have reported that the stem bark of *E. chlorantha* possesses wide spectrum antimicrobial and antimalarial activities (Adesokan*et al.,* 2008; Odugbemi *et al.,* 2007). The anti-pyrogen, anti-viral and anti-bacterial activity of this plant has also been investigated (Agbaje and Onabanjo, 1998; Taiye *et al.,* 2011). The plant is commonly used in Cameroon in form of a decoction for gastric ulcer therapy, and it has

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been demonstrated that a protoberberine alkaloid extracted from *Enantia chlorantha* has anti-ulcerogenic effects on gastric ulcers (Tan *et al.,* 2000). It is used in the treatment of hypoglycaemia, typhoid fever. The stem bark is also used for treating leprosy spots, as haemostatic agent and uterus stimulant (Gill, 1992). An anti-sickling compound has also been isolated from the ethanolic extract of the plant (Ejele *et al.,* 2012).

The phytochemical composition of the tree bark extract of *Enantia chlorantha* reveals that it contains compounds such as saponins, phenols, alkaloids, flavonoids, tannins and steroids similar to those found in other well-known corrosion inhibitors that can absorb on the metal surface via the lone pair of electron present in the heteroatom e.g. (N, S and O), which abound in these constituents (Lebrini *et al.,* 2013; Dawodu *et al.,* 2014; Singh and Quraishi, 2017). This could be thought to create a barrier for charge and mass transfer leading to a decrease in the level of interaction between the metal surface and the corrosive environment. This in turn decreases the corrosion rate of the metal.

Therefore, this study is focused on the utilization of *Enantia chlorantha* extract in the inhibition of pipeline steel from corrosion in acidic system.

MATERIALS AND METHODS

Metal Coupons and Reagents Preparation:A pipeline steel sheet of 0.5cm thickness was obtained and cut into coupons of dimension 2cm by 3cm at the University of Port Harcourt Science and Engineering workshop, Choba. A hole of 2mm was drilled at the upper centre of each coupon to allow the passage of polymeric thread which enabled suspension during immersion. Thereafter, the coupons were polished with different grades of abrasive paper (200 to 2000 grits), washed in distilled water, degreased in ethanol and further rinsed in acetone to remove any residue and quicken drying. The coupons were allowed to dry to constant weight and stored in a desiccator to avoid contamination before use.

*Reagents:*Sulphuric acidand other reagents used were obtained from BDH chemical Ltd Poole England and was used without further purification.

Test additive preparation (Enantia chlorantha extract): Fresh samples of the *Enantia chlorantha* tree bark was obtained from herbal medicine sellers at Rumuokoro market, Port Harcourt and identified at the Plant Science and Biotechnology department, University of Port Harcourt. The sample was washed and sun-dried to constant weight. The dried sample was milled with a grinder in order increase the surface area. 500 g of the dried sample was weighed using a mettle AE 160 weighing balance and soaked in 1000 ml flask; absolute ethanol was added to sufficiently cover the surface for 72 hours. It was then filtered to obtain a deep yellowish solution which was later concentrated using a rotary evaporator. The Slurry extract was further dried in a thermostatic water bath between 30 to 40 ºC. The extract was stored in a tight analytical container in a cool dry environment and different serial diluents of the extract were prepared with 0.5 M H_2SO_4 solution. The additive concentration ranged from 0.5 g/L to 2.5 g/L with a differential of 0.5.

Gravimetric Determination:The pre-cleaned metal coupons were weighed before commencement of the experiment. Each of the metal coupons were labelled with a rubber thread and masking tape and dipped in a 250 ml beaker containing 200 ml of one of the five different test solutions prepared earlier. The test was carried out at 30 ± 1 ºC. All the experiments were carried out under total immersion and unstirred condition. The sixth coupon was dipped in a 250 ml beaker containing 200 ml 0.5 M H_2SO_4 solution with no additive and was used as the control for the experiment. The weight loss was determined by retrieving the coupons at 4 hours interval for seven consecutive times (28 hours). Prior to measurement, each coupon was washed in distilled water using a bristle brush, rinsed in ethanol and dried in acetone and re-weighed every 4 hours. The difference between the initial weight (before immersion) and final weight (after immersion) was recorded as the weight loss. The experiment was repeated at 40 and 60 ºC using a thermostatic water bath. For this set of experiment, the coupons were retrieved at 2 hours interval for 14 hours with the sixth coupon used as blank for the experiment. All the experiments were carried out in triplicate to ensure reproducibility. The average of the values was used for subsequent calculations.

RESULTS AND DISCUSSION

Gravimetric Behaviour of Pipeline Steel in Sulphuric Acid with and without Enantia chlorantha: The gravimetric behaviour-weight loss of pipeline steel in 0.5 M H_2SO_4 with and without varying concentrations of *Enantia chlorantha* bark (ECB) extract was studied at different temperatures and the results presented in Figures 1 to 3. From Figure 1, the corrosion of Pipeline steel in acidic environment at 30 ± 1 ºC was continuous throughout the experimental duration. This has been earlier reported and is in agreement with the second law of thermodynamics (Ngobiri and Okorosaye-Orubite, 2017).

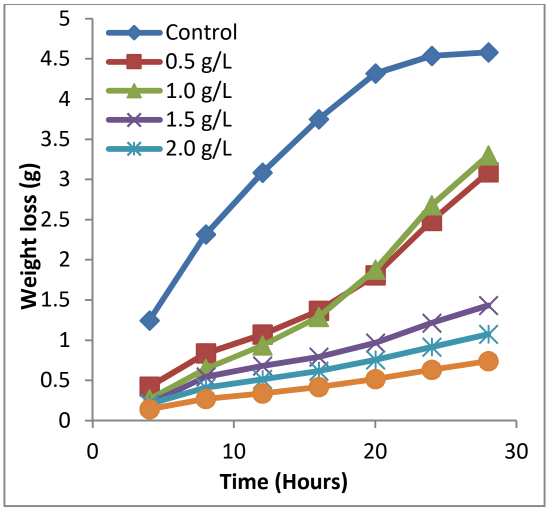

Fig. 1: Variations in weight loss with time for pipeline steel coupons in 0.5 M H_2SO_4 solution containing different concentrations of *Enantia chlorantha* at 30 ºC

The introduction of *Enantia chlorantha* bark (ECB) extract clearly reduced the weight loss as can be seen by the significant difference between the control and the cells with ECB extract. The decrease in weight loss increased with increase in the extract concentration and tends to decrease with time for lesser concentrations of the extract. This trend has been severally reported (Ngobiri and Okorosaye-Orubite, 2017). As the concentrations of ECB increased, the line tend to be straight and parallel to time axis suggesting the ability of the extract to overcome all barriers to the inhibition process. The effect of rise in temperature on the corrosion process was studied at 40 ± 1 and 60 ± 1 ºC and the results presented in Figures 2 and 3 respectively.

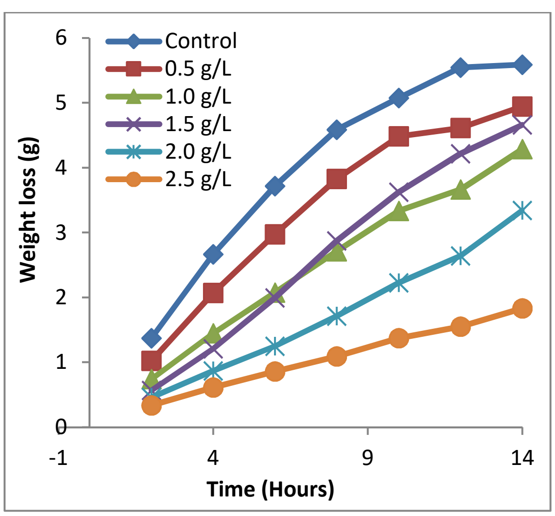

Fig.2: Variations in weight loss with time for pipeline steel coupons in 0.5 M H_2SO_4 solution containing different concentrations of *Enantia chlorantha* at 40 ºC

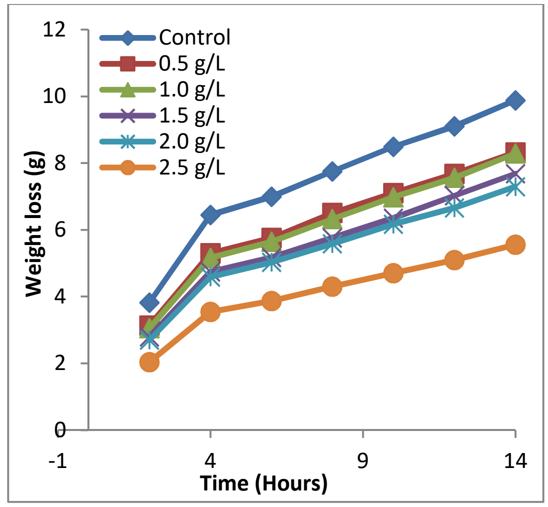

Fig.3: Variations in weight loss with time for pipeline steel coupons in 0.5 M H_2SO_4 solution containing different concentrations of *Enantia chlorantha* at 60 ºC

Similar corrosion and inhibition trends were also noticed as in the previous determination. However, the weight loss obviously increased with rise in temperature though trend lines were not parallel. All these can be attributed to the increase in kinetic energy from the supply of heat to the corrosion system with consequent increase in rate of weight loss and corrosion. However, the results show the ability of ECB extract to decease the dissolution of steel pipe in acidic environment.

Corrosion inhibition efficiency:The corrosion inhibition capacity and of ECB extract was analysed for corrosion inhibition efficiency and surface coverage θ by applying equations 1 and 2.

$$IE\ (\%) = \left(1 - \frac{CR_{inhibition}}{CR_{blank}}\right) \times 100 \quad (1)$$

$$\theta = 1 - \frac{CR_{inhibition}}{CR_{control}} \quad (2)$$

Where IE = inhibition efficiency, $CR_{inhibition}$ = corrosion rate for inhibition, $CR_{control}$ = corrosion rate for control, θ = surface coverage

The results obtained as shown in Figure 4 showed an increase in corrosion inhibition efficiency with increase in concentration of ECB extract. This trend as reported by many researchers revealed the presence of phytochemical compounds in the extract (Obot *et al.,* 2012; Mejeha *et al.,* 2012; Ngobiri *et al.,* 2013; Dharmaraji *et al.,* 2017). However, the corrosion inhibition efficiency decreased with increase in extract temperature i.e. from 30 ºC to 60 ºC. Also, the surface coverage increased with increase concentration of the extract.

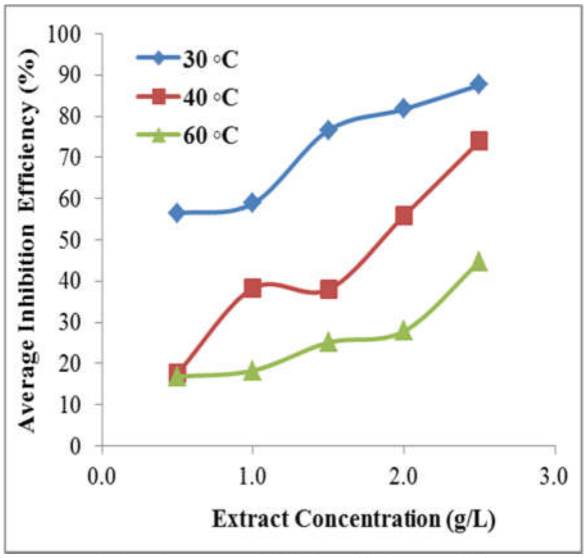

Fig.4: Variations in average inhibition efficiency at different ECB extract in 0.5 M H_2SO_4

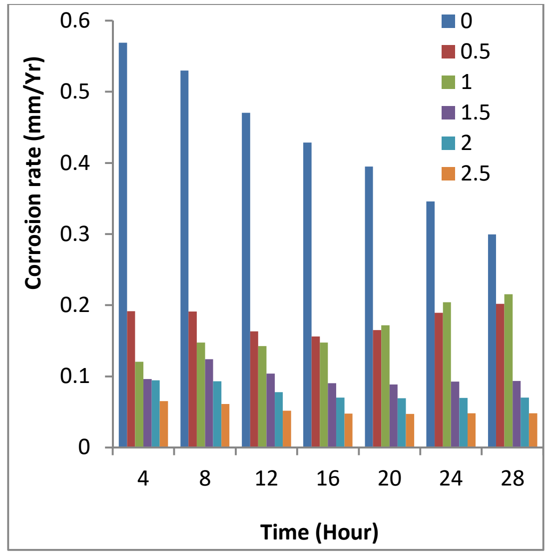

Fig.5: Corrosion rate of Pipeline steel in H_2SO_4 with and without ECB extract at 30 ºC

This observation may be due to desorption of the phyto-compounds from the steel surface (Lebrini *et al.,* 2013).

Corrosion rate: The corrosion rate (CR) for the pipeline steel in 0.5 M H_2SO_4 environment with and without varying concentration of ECB was calculated from the weight loss data using Equation 1. The data obtained was plotted as a function of time and extract concentration. The plots are shown in Figures 5 and 6.

$$CR_{(\text{mm per year})} = \frac{87.6\,\Delta w}{DAT} \qquad (3)$$

Where Δw = the weight loss, D = the density of steel (g/cm^3), A = the area of the coupon in (cm^2) and T = exposure time (h).

The corrosion rate decreased with increase in concentration of ECB extract as shown in Figures 5 and 6 and a reverse trend as temperature increased. This trend can be attributed to increase in the phytochemical constituents of the extract and consequent increase in surface coverage. This must have resulted in more effective blocking of corrosion active sites on the pipeline steel surface. The effect of temperature rise can again be attributed to increased kinetic energy of the system (Cang *et al.,* 2013).

Corrosion rate constant and Material half-life: The corrosion rate constant (K) and material half-life ($t_{1/2}$) for the corrosion of pipeline steel in acidic environment in the presence and absence ECB was evaluated from the weight loss data using equations 4 and 5:

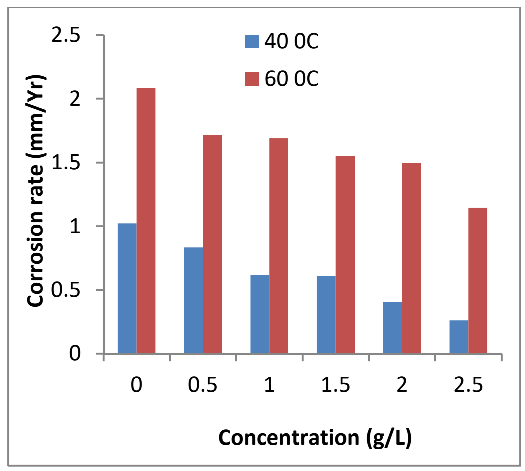

Fig.6: Corrosion rate of Pipeline steel in H_2SO_4 with and without ECB at 40 and 60 ºC

$$K = \frac{2.303}{t}\log\frac{w_i}{w_f} \qquad (4)$$

While the half-life $t_{1/2}$ was calculated from K as:

$$t_{\frac{1}{2}} = \frac{0.693}{k} \qquad (5)$$

Where w_i and w_f are initial and final weight respectively, t is time.

The results obtained were plotted with concentration and shown in Figures 7 and 8 for 30 ºC (303 K) and 60 ºC (333 K) respectively. The result obtained showed that ECB surface coverage had a good relationship with the concentration. This could also be attributed to the coverage and blocking of corrosion active sites on the metal surface by ECB molecules.

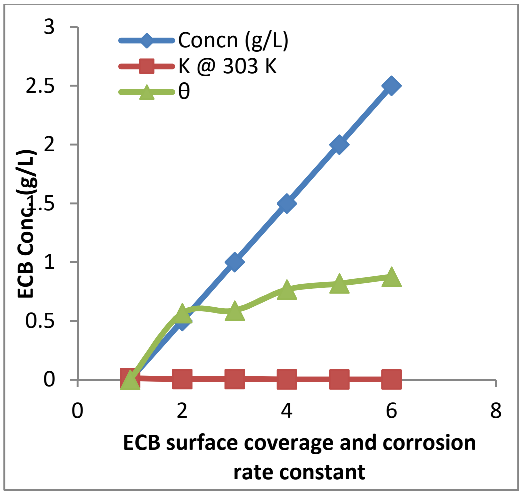

Fig.7: ECB concentration against ECB surface coverage and corrosion rate constant for pipeline steel corrosion in acidic environment at 30 °C (303 K)

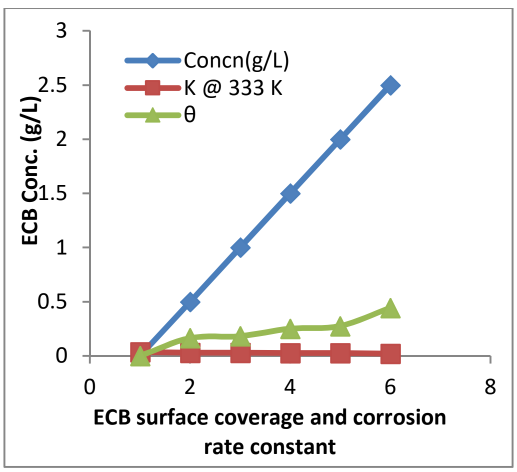

Fig.8: ECB concentration against ECB surface coverage and corrosion rate constant for pipeline steel corrosion in acidic environment at 60 °C (333 K)

Table 1: Material half life of pipeline steel in acidic environment at varying concentrations of ECB.

ECB Conc. (g/L)	$t_{1/2}$ @ 303 K	$t_{1/2}$ @ 313 K	$t_{1/2}$ @ 333 K
0.0	64.71	44.16	19.43
0.5	136.10	53.21	22.61
1.0	160.56	73.45	24.52
1.5	265.82	72.40	25.10
2.0	347.58	112.60	25.52
2.5	498.65	182.48	34.26

Though corrosion rate constant plot is parallel to surface coverage, they varied inversely. The data for the material half-life was evaluated and presented in Table 1. The material half-life varied directly with ECB concentration. Therefore, the corrosion rate constant K is the inverse of the material half-life ($t_{1/2}$). This also confirms the corrosion inhibiting effect of ECB extract.

Conclusions: The inhibition efficiency of *Enantia chlorantha* extract increases with increase in extract concentration and decreases with increase in temperature as a result of greater kinetic energy of the steel molecules at higher temperature.This study also reveals that the presence of *Enantia chlorantha* extract increased the material half-life in acidic environment.The material analysis of *Enantia chlorantha* extract shows that it is a potential corrosion inhibitor for pipeline steel in acidic environment.

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