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Eco-friendly Corrosion Inhibitor from *Tagetes patula L.* for Aluminium alloy (3SR) in Acid Fluid Used in Industrial Operations

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Abstract
The ability of Tagetes patula L. leaf extract (TPLE) as green corrosion inhibitor for acid corrosion of aluminium in acid fluid (1 M HCl) was studied using chemical technique. TPLE extract inhibited the acid corrosion of Al significantly, with about 90 % efficiency at the highest concentration of the extract. The adsorption of the inhibitor molecules on aluminium surface was found to obey Langmuir adsorption isotherm with ΔG^0_{ads} *value of 13.01 k J* mol^{-1}.

Keywords: *Tagetes patula L.*, Acid fluid, Eco-friendly inhibitor, Aluminium, Adsorption.

Introduction
Acid fluids are widely used in oil well stimulation, oil well cleaning, industrial acid cleaning, acid pickling, cleaning of oil refinery, heat exchanger and vapour liquid system [1-7]. HCl solution is the acid fluid of choice for these industrial processes. The use of corrosion inhibitors is one of the most practical, effective and economic methods to protect metals in acid fluid environment encountered in the industry. A number of industrial inhibitors of metals in acid solutions are based on organic compounds containing heteroatom of oxygen, nitrogen or sulphur [1-5, 7-9]. The corrosion protection by inhibitors is based mostly on the modification of metal surface by adsorption of inhibitor molecules and the subsequent formation of a protective layer [1,8, 9,10]. However, some of these inhibitors are toxic and non-biodegradable [7, 8] and this limit application. Consequently, attention has been focused on the need to design and develop non-toxic corrosion inhibitors from plants to replace toxic ones for sustainable development. This is because plants serve as incredibly rich sources of naturally synthesized chemical compounds that are environmentally acceptable, biodegradable, inexpensive, readily available and renewable source of materials [1,3, 8]
More recently, we reported the inhibition of aluminium corrosion in HCl solution using extracts of *Aloe vera* [8], *Gossipium hirsutum* L.[11], *Cocos nucifera* L. [1,12], *Delonix regia* [13] and *Citrus paradise* [14].The inhibitory action of the extracts from these plants was attributed to the presence of organic compounds and the blocking of the metal surface via adsorption of these organic compounds in acid solutions.
Tagetes patula L .(French marigold) is a medicinal plant which is widely distributed in Africa, Europe, North and South America. The crude extracts of the plant have shown nematocidal, antimicrobial, insecticidal and antitumor activities. The tagetes oil is used for the compounding of high-grade perfumes [15-17]. However, literature search reveals that the use of *T. patula* L. as corrosion inhibitor for aluminium in acid fluid used in industrial operations is yet to be explored.

Materials and Methods
The chemical composition and preparation of aluminium alloy 3SR test specimens of dimensions 5 x 2 x 0.04 cm were as reported in previous communications [18]. HCl was of analytical grade and 1 M HCl was employed as the aggressive solution for this study. Stock solution of the plant was prepared by refluxing weighed amount (1 g) of the dried powder leaf of *T. patula* L. for 1 h in 100 ml 1 M HCl solution. The refluxed solution was allowed to stand for 8 h, filtered and stored. The filtrate was diluted with the appropriate quantity of 1 M HCl solution to obtain inhibitor test solutions of 0.2, 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0% v/v concentrations. The procedure for weight loss determination was similar to that reported earlier [1-3, 18]. According to this method [1-3, 18], previously weighed aluminium coupons were immersed in 100 ml open beakers containing 50 ml of 1 M HCl (blank) and then with addition of different extract concentrations to the 1 M HCl (0.2 – 5.0% v/v) at 30 ^oC . The variation of weight loss was monitored after 30 min immersion per coupon progressively for a total of 150 min at 30 ^oC as presented in Fig. 1. The weight loss was calculated in mg as the difference between the initial weight and the final weight after the

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removal of the corrosion product. The experimental readings were recorded to the nearest 0.0001 g on a Mettler digital analytical balance (digital analytical balance with sensitivity of ±1 mg). Duplicate experiments were conducted for each concentration of the extract. The average weight loses of duplicate experiments as presented in Figure 1 were taken as the weight loss of aluminium coupon for each of the concentration.

Results and Discussion

The results obtained are presented in Figures 1, 2 and 4 for different concentrations of the extracts in 1 M HCl solution from weight loss measurements.

The material loss (mg/cm^2) of aluminium specimens as a function of the extracts concentration in 1 M HCl solution monitored at 30^{o}C is presented in Figure 1. The values of percentage inhibition efficiency (% I) and surface coverage (θ) were determined from the weight loss using the following equations [1,3, 8].

$$\% I = [w_u - w_e / w_u] \times 100 \quad (1)$$

$$\theta = \% I / 100 \quad (2)$$

where w_u and w_e are the weight losses of the aluminium coupon without and with the extract at 30^o C, respectively.

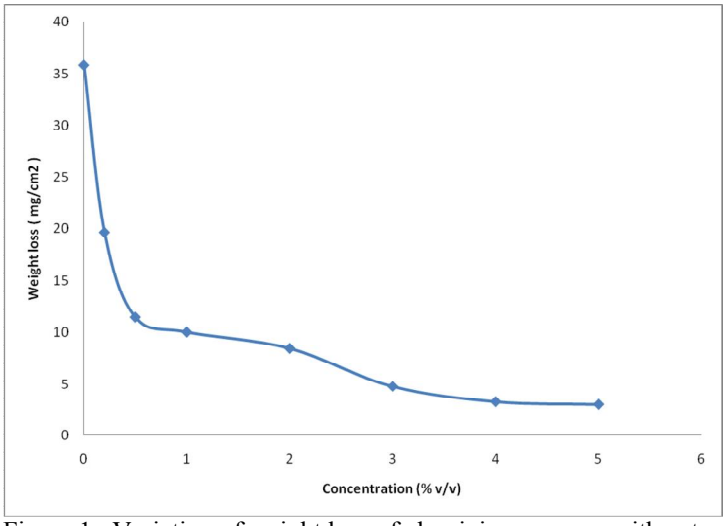

Figure 1. Variation of weight loss of aluminium coupon with extract concentration at 30^o C.

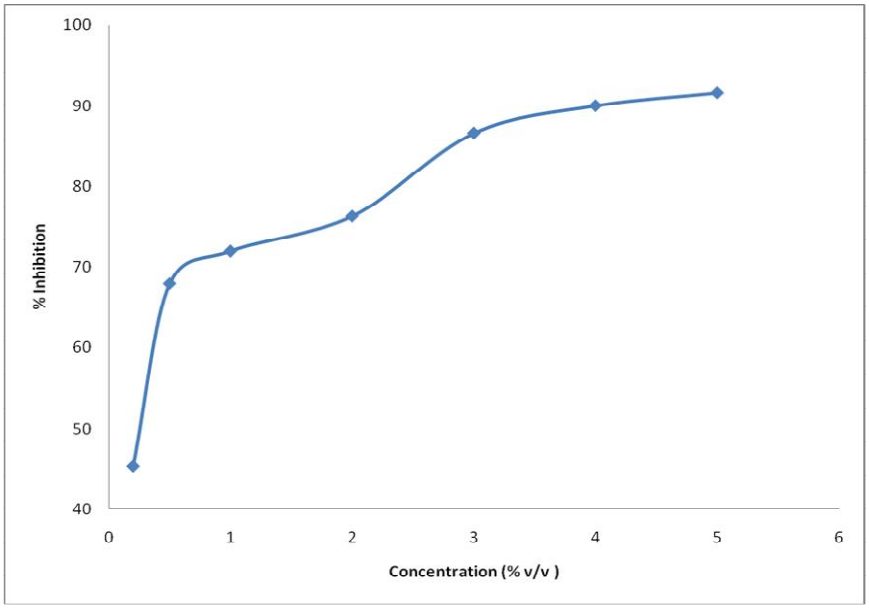

Figure 2. Variation of percentage inhibition efficiency with extract concentration at 30^o C.

It is evident in Figure 1 that the introduction of the extracts at different concentrations to the HCl solution decreased the value of weight loss from the surface of the Al. This result indicates that the extract acts as acid inhibitor of Al corrosion in HCl solution at the studied concentrations. As presented in Figures 1 and 2, the material loss decreased with increasing concentration of the extracts in HCl solutions and the inhibition efficiencies increase with increasing extract concentration. This indicates that the inhibition is due to the adsorption of inhibitor`s molecule onto Al surface and Tagetes extract acts as an adsorption inhibitor. The inhibitory effect of *T.patula L.* extract is attributed to the presence of organic compounds such as terpenes (Figure 3) in *T.patula L.* chemical constituents. The adsorption of such compounds on the Al surface leads to reduction in surface area that is available for the electrochemical process of corrosion on the metal surface, thus slowing down the electrochemical process of corrosion.

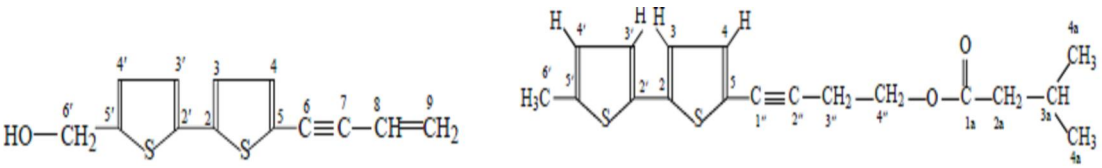

Figure 3. Examples of chemical structures of terpine in *T. patula* L.

Figure 4 confirms that the inhibitory effect is due to the adsorption of the organic compounds in the extracts and the adsorption obeys the Langmuir adsorption isotherm. This is because (Figure 4) a straight line is obtained, when C/θ is plotted against C and the linear correlation coefficient of the fitted data is good (0.996).

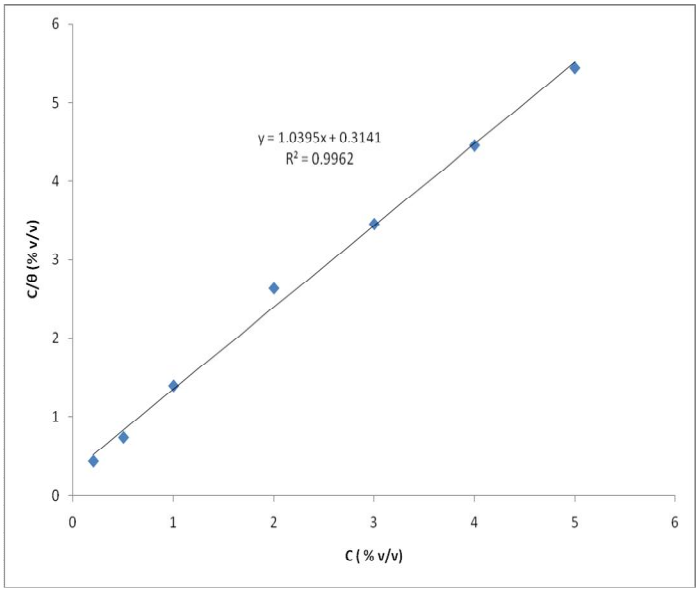

Figure 4. Langmuir adsorption model on Al surface of the extracts 1 M HCl solution M at 30^{o} C.

Value of standard free energy of adsorption, ΔG^{0}_{ads} was obtained from the reciprocal of the intercept of Figure 4, with the help of an equation used in Refs. [1,2]. The value of ΔG^{0}_{ads} for the inhibition of aluminium in the acid fluid was found to be 13.01 kJ mol^{-1} at 30^{o} C.

Value of standard free energy of adsorption, ΔG^{0}_{ads} indicates that the adsorption of the inhibitor molecules is a spontaneous process [1,2]. The calculated value of ΔG^{0}_{ads} supports the mechanism of physisorption for the inhibitor action in HCl solution.

Conclusions: The leaf extract of *T. patula* L. can be used as non-toxic corrosion inhibitor for aluminium corrosion in acid fluid (HCl solution). *T. patula* L. extract acts as inhibitor for the corrosion of aluminium in 1 M HCl solution. The inhibitory efficiency increased with increase in extract concentration. The adsorption of the inhibitor molecules on aluminium surface follows the Langmuir adsorption isotherm.

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