

# Corrosion Inhibition of *Ocimum tenuiflorum* (Tulasi) Leaves Extract as a Green Inhibitor for Zinc in H<sub>2</sub>SO<sub>4</sub>

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## ABSTRACT

The corrosion inhibition properties of *Ocimum tenuiflorum* (Tulasi) leaves extract as a potential green inhibitor of zinc corrosion in H<sub>2</sub>SO<sub>4</sub> have been investigated employing gravimetric and thermometric techniques. The results show that different concentrations of the *Ocimum tenuiflorum* extract have inhibited zinc corrosion and that the inhibition efficiency has varied with the concentration of extract and temperature of experimental corrosion half-cell.

**Keywords:** Corrosion; inhibition; zinc; *Ocimum tenuiflorum*; H<sub>2</sub>SO<sub>4</sub>.

## INTRODUCTION

The use of inhibitors is one of the most practical methods for protection against corrosion. Sulphuric acid is widely used in industry, acid pickling, industrial acid cleaning, acid descaling and oil-well cleaning. The use of green inhibitors for the control of corrosion of metals<sup>1</sup> and alloys which are in contact with aggressive environment is a growing practice<sup>2</sup>. Large numbers of organic compounds are being tested for their corrosion inhibition potentials of different metals. All these studies unanimously show that organic compounds especially those containing N, S and O show corrosion inhibition efficiencies. The influence of organic compounds containing nitrogen on the corrosion of mild steel in acidic media has been studied<sup>3-5</sup>. Most organic inhibitors act by adsorption on the metal surface<sup>6-8</sup>. It has been known that efficient inhibitors should possess plentiful of  $\pi$  electrons and unshared electron pairs on nitrogen atoms of the inhibitors<sup>2</sup> which will be given to the vacant *d*-orbital of the metal, and by means of transfer of electrons, chemical adsorption may occur on the surface. Thus, the corrosion process may be suppressed by the protective film of inhibitor on the metal surface. Organic molecules from different plant extracts have become important as environmentally acceptable, readily available and renewable sources for a wide range of corrosion inhibitors<sup>9</sup>. They are rich sources of environment friendly and biodegradable ingredients which have relatively high inhibition efficiencies<sup>10</sup> and have been hence termed '*green inhibitors*'<sup>11</sup>.

Examples are the *Azadiracta Indica* (Neem) and *Capparis deciduas*<sup>12</sup> plants that have been tested for their corrosion inhibition for aluminium in acidic medium. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some research groups namely Abdel -Gaber *et al.*, Khamis *et al.*, Uomren and Ebenso, Okafor and Ebenso, Bendahou et al. and Kliskic et al., running through references 13 to 18, respectively. Incidentally, testing natural organic substances for their corrosion inhibition<sup>19, 20, 21</sup> from so far untested plants extracts is a key area of research.

## LITERATURE REVIEW

### Zinc corrosion inhibition

Zinc is a metal with numerous industrial applications and is mainly used for the corrosion protection of steel<sup>22</sup>. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous. Looking at its increasing use, the study of corrosion inhibition is of paramount importance. The dissolution behaviour of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen and sulphur-containing organic compounds. Such compounds contain electron-donating groups that decrease the corrosion rate by increasing the hydrogen over voltage on the corroding metal<sup>23</sup>. Studies of the effect of organic additives on the corrosion rate of zinc have been the subject of many investigators<sup>24, 25</sup>. The efficiency of aldehydes and amino acids as inhibitors of corrosion for different metals in different metals in different corrosive environments has been studied by several workers<sup>24</sup>, and their inhibition efficiency is due to the formation of a protective layer or film on the metallic surface. The role of this film is to isolate the corroding metal from the corrosive medium<sup>27</sup>.

### *Ocimum tenuiflorum* - General properties

Tulsi, the "Queen of Herbs", is the most sacred herb of India. Tulsi has been revered in India for over five thousand years, as a healing balm for body, mind and spirit, and is known to bestow an amazing number of health benefits. There are three varieties of Tulsi namely, Rama Tulsi (*Ocimum sanctum*), Krishna Tulsi (*Ocimum tenuiflorum*) and Vana Tulsi (*Ocimum gratissimum*). Each variety lends its own distinct and characteristic taste that contributes to the delicious flavour and aroma of our blend. The *Ocimum* genus belonging to the Lamiaceae family<sup>28</sup> is characterized by a great variability of both morphology and chemo types, the ease of cross-pollination leads to a large number of subspecies, varieties and forms, which differ in essential oil composition and morphological characters. The aromatic and morphological characters, determined by genotype are greatly influenced by environmental conditions and agronomic techniques. Among all the species, *Ocimum* spp., has the most economic importance and is cultivated and utilized throughout the world, because of the continuous and increasing demands for their products from the local and foreign markets. The aromatic leaves are used fresh or dried as a flavouring agent for foods, confectionary products<sup>31</sup>. Traditionally, *Ocimum* has been employed in folk medicine for its carminative, stimulant and antispasmodic

properties<sup>30,31</sup>. The essential oils, mainly used in food industries, perfumery, also possess antimicrobial and immunomodulatory potential<sup>32</sup>, and some of its components<sup>33</sup>, such as camphor and 1,8 -cineol are known to be involved as allelopathic agents . Various uses are attributed to different parts of the plant in indigenous system of medicine and homoeopathy. It is also recognized as a febrifuge, antimalarial<sup>28</sup> and anti-diabetic<sup>34</sup>.

### **Chemical composition of *Ocimum tenuiflorum***

Omer *et al.*<sup>31</sup> performed a detailed chemical analysis of the *Ocimum tenuiflorum* species and found that more than 40 chemical organic and aromatic molecules could be isolated from the extracts. The main chemical constituents in *O. tenuiflorum* were grouped as essential oils (0.516 -0.596%), total carbohydrates (11.87 -11.50%), total flavonoids (0.735-0.945%) and proline (0.28-0.536 mmol/g leaves fresh weight). Omer *et al.*<sup>29</sup> further determined that the essential oil of *O. tenuiflorum* contained higher amount of linalool (39.39-55.26%) and moderate amounts of methyl chavicol (0-6.66%), nerol (0.48-8.0%), geraniol (0.26-1.75%) and citral (4.26-6.79%). Another recent analysis of the chemical constituents in the essential oils of *O. tenuiflorum* by Vani *et al.*<sup>35</sup> revealed the presence of  $\alpha$ -humulene (0.71%), germacrene D (2.11- 4.91%),  $\beta$ -elemene (1.59-6.35%), methyl eugenol (36.47-76.27%) and  $\beta$ -caryophyllene (8.71-56.63%). The essential oils of the air-dried aerial parts of *O. tenuiflorum* L.f., harvested in four stages of vegetation, were isolated by hydrodistillation and analyzed by capillary gas chromatography (GC), GC/MS, and <sup>1</sup>H-NMR by Kicel *et al.*<sup>36</sup>. It was found that the content of the main constituents were  $\beta$ -bisabolene (13-20%) 1,8-cineole (9-33%) and methyl chavicol (2-12%) and which varied during development of the plant.

## **MATERIALS AND METHODS**

### **Preparation of *Ocimum tenuiflorum* leaf extract stock solution**

Stock solution of the *O. tenuiflorum* extract was prepared by boiling 20-25 g of air-dried *O. tenuiflorum* adult leaves in deionised water and left overnight. The *O. tenuiflorum* leaves were air-dried earlier in natural sunlight until the final mass became constant. The contents were then filtered and the resulting solution was kept in a refrigerator at low temperatures of 2-3°C in order to prevent the contents of the extract from being altered due to the chemical, physical, and biological reactions it might otherwise undergo<sup>37</sup>.

### **Specimen preparation**

Rectangular specimen sheets of zinc were mechanically pressed cut to form different coupons, each of dimension 5.0 cm long, 2.5 cm wide and 0.040 cm thick. Each coupon was degreased by washing with ethanol, dried in acetone and preserved in a dessicator. All reagents used for the study were Analar grade and double distilled water was used for their preparation. Specimens containing a small hole of 2 mm diameter near the upper edge were used for the determination of corrosion rate (**CR**).

**Inhibition efficiency (I) and degree of surface coverage ( $\theta$ )**

The mass loss method was employed for a room temperature of 303K. In this procedure, the mass loss of the metal in uninhibited (no extract) and inhibited solutions (with extract) were measured and recorded for an immersion time of 30 minutes in 50mL of solution. From these data, the inhibition efficiency (%I) and degree of surface coverage ( $\theta$ ) were calculated using Eq. (1) and Eq. (2), respectively<sup>38</sup>.

$$\%I = \left(1 - \frac{\Delta M_i}{\Delta M_u}\right) \times 100 \quad \rightarrow (1)$$

where  $\Delta M_u$  and  $\Delta M_i$  are the mass loss of zinc in uninhibited solution and inhibited solution, respectively.

$$\theta = \left(1 - \frac{\Delta M_i}{\Delta M_u}\right) \quad \rightarrow (2)$$

The CR in mmpy (millimetres per year) has been calculated from Equation 3.

$$CR = \frac{(Mass\ Loss) \times 87.6}{(Area)(Time)(Metal\ Density)} \quad \rightarrow (3)$$

where mass loss is expressed in mg, area is expressed in cm<sup>2</sup> of metal surface exposed, time is expressed in hours of exposure and metal density is expressed in g/cm<sup>3</sup> and 87.6 is a conversion factor.

**Thermometric method**

This was also carried out as reported elsewhere<sup>39,40</sup>. In this technique the immersion of a single specimen measuring 5.0 x 2.5 x 0.04 cm was analyzed in a reaction vessel containing 50 mL of test solution for an immersion time of 30 minutes. Temperature changes were measured at interval of one minute using a thermometer with a precision of  $\pm 0.2^\circ\text{C}$ . The temperatures increased slowly at first and then rapidly and finally attained a maximum temperature. This temperature rise was recorded and used to calculate the Reaction Number (RN) from Eq. (4)

$$RN = \frac{T_m - T_i}{t} \quad \rightarrow (4)$$

where  $T_m$  is the maximum temperature attained by the system and  $T_i$  is the initial temperature ( $^\circ\text{C}$ ) and  $t$  is the time required to reach the maximum temperature in minutes. From the above, the inhibition efficiency (I%) of the used inhibitor was computed using Eq. (5).

$$\%I = \left(1 - \frac{RN_i}{RN_u}\right) \times 100 \quad \rightarrow (5)$$

where  $RN_u$  is the reaction number in uninhibited solution and  $RN_i$  is the reaction number for the solution containing the *O. tenuiflorum* extract as green corrosion inhibitor. The pH value in all experiments was measured before and after equilibrium but the solution was not buffered in order to simulate the real situation. There was no evidence of precipitation.

## RESULTS AND DISCUSSION

Table 1 shows values of corrosion rate (**CR**) of zinc in all the concentrations of H<sub>2</sub>SO<sub>4</sub> studied. It may be inferred that the corrosion rate increases with increase in H<sub>2</sub>SO<sub>4</sub> concentration. Table 2 shows the corrosion rate and reaction numbers (**RN**) for the corrosion of zinc at 2.0N H<sub>2</sub>SO<sub>4</sub> in the absence and presence of *O. tenuiflorum* extract. An increase in the concentration of the inhibitor generally retards the corrosion rate of zinc in the solutions. This is supported from the overall decreasing change in mass loss taking place (Figure 1) at a particular acid concentration corresponding with an increase in inhibitor concentration. The fluctuating losses in mass above an extract concentration of 2.5 mg · L<sup>-1</sup> could be due to the subsequent heterogeneity of the zinc surface after the corrosion process is initiated by the acid attack. The surface heterogeneity thereafter strongly affecting the surface coverage by some adsorbed hydrogen gas<sup>41</sup> may have caused the rates of corrosion and corrosion inhibition reactions in the cathodic (active) sites on the zinc surface to vary. Table 3 shows values of inhibition efficiency of the different concentrations of *O. tenuiflorum* extract at 303K and 333K for both the gravimetric and thermometric methods. For both approaches, the corrosion inhibition is larger at 303K than at 333K, thus supporting that temperature affects the corrosion of zinc.

### Effects of concentration and temperature

From Tables 1 and 2, it is found that the rate of corrosion of zinc is affected by concentration of H<sub>2</sub>SO<sub>4</sub>, temperature, and concentration of the *O. tenuiflorum* extract. The rate of zinc corrosion increases as the concentration of H<sub>2</sub>SO<sub>4</sub> increases and also increases as the temperature is increased. The increased corrosion rate with the rise in temperature may be accounted as a result of an increase in the transportation action of the acid proton (H<sup>+</sup>) to the zinc surface, so that the reduction reaction at the cathode in the microscopic corrosion cells is enhanced in the absence of the inhibitors<sup>27</sup>. However, in the presence of inhibitors in sufficiently large concentrations, the percentage inhibition efficiency increased with rises in temperature. In acid solution the used inhibitors exist as protonated species, which can adsorb on the cathode sites of zinc and decrease the evolution of hydrogen<sup>42</sup>. The rate of cathodic reaction, and hence corrosion, is thus reduced in the presence of inhibitors. The mass loss taking place and recorded at the different concentrations of the *O. tenuiflorum* extract (Figure 1) are lower than that of the blank solution indicating that different concentrations of the extract succeed in retarding the corrosion of zinc. It is most likely due to adsorption of the active corrosion inhibiting chemical molecules in the *O. tenuiflorum* extract on the surface of zinc metal. Figure 1 also shows the mass loss plots for the corrosion of zinc in the presence of different concentration of the extract at 303K and 333K. Comparing the plots for the two temperatures, it is deduced that at a fixed concentration of the inhibitor and a fixed acid concentration, the mass loss taking place at 333K is higher than that occurring at 303K indicating that the inhibition efficiency (gravimetric method) of *O. tenuiflorum* extract decreased with increase in temperature. The decrease may be due to some kind of competition

between forces of adsorption and desorption the surface of the zinc metals by certain specific molecules in the extract active in the corrosion inhibition reactions in the different layers<sup>43</sup> and cathodic sites on the zinc surface<sup>27</sup>. Figure 2 shows the variation of inhibition efficiency against the different concentrations of *O. tenuiflorum* extract at 303K and 333K. The significant difference between inhibition efficiency of *O. tenuiflorum* extract obtained at 303K and 333K are two-tiered. For the lower concentrations of the extract (2.273, 4.167, 5.769 and up to 7.143 mg·L<sup>-1</sup>), the inhibition efficiency is seen to decrease with an increase in temperature, while for the relatively higher concentration of 8.333 mg·L<sup>-1</sup> and 9.375 mg·L<sup>-1</sup>, the inhibition efficiency is higher at 333K than 303K. For the concentrations studied presently, these observations suggest that for concentrations of the *O. tenuiflorum* extract lower than 7.143 mg·L<sup>-1</sup>, the mechanism of adsorption of the inhibitor molecules on the zinc surface may be by physical adsorption, and for concentrations of the *O. tenuiflorum* extract above 8.333 mg·L<sup>-1</sup>, the mechanism of adsorption may be by chemical adsorption. This is in accordance with the statement of<sup>39,44</sup> stating that for the physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature while for the chemical adsorption mechanism, values of inhibition efficiency increase with temperature.

**Table-1: Corrosion rate (gravimetric) and reaction number (thermometric) for corrosion of zinc in H<sub>2</sub>SO<sub>4</sub> at 303K**

Concentration of H <sub>2</sub> SO <sub>4</sub> (N)	CR (mmpy)	RN
0.5	1.181	1.8
1	1.317	4.5
2	1.479	4.9

**Table-2: Corrosion rate (gravimetric) and reaction number (thermometric) for corrosion of zinc in 2N H<sub>2</sub>SO<sub>4</sub> solutions containing extract**

Concentration of <i>O. tenuiflorum</i> extract in 2.0N H <sub>2</sub> SO <sub>4</sub> (mg·L <sup>-1</sup> )	RN 303K	CR (mmpy) 303K	CR (mmpy) 333K
Uninhibited	4.9	1.479	1.725
2.273	1.5	0.5678	1.039
4.167	1.3	0.4697	0.7459
5.769	1.4	0.3698	0.5766
7.143	1.4	0.2833	0.3893
8.333	1.3	0.3077	0.3432
9.375	1.3	0.4394	0.2301

**Table-3: Inhibition efficiency (%I) and degree of surface coverage from gravimetric and thermometric methods for 2.0N H<sub>2</sub>SO<sub>4</sub>**

Concentration of <i>O. tenuiflorum</i> extract (mg·L <sup>-1</sup> )	Gravimetric		Thermometric	
	303K	333K	303K	333K
2.273	49.25	26.25	69.39	71.25
4.167	62.69	52.5	73.46	41.25
5.769	70.15	67.5	71.43	57.5
7.143	77.61	75	71.43	45
8.333	73.13	76.25	73.46	37.5
9.375	70.15	86.25	73.46	31.25

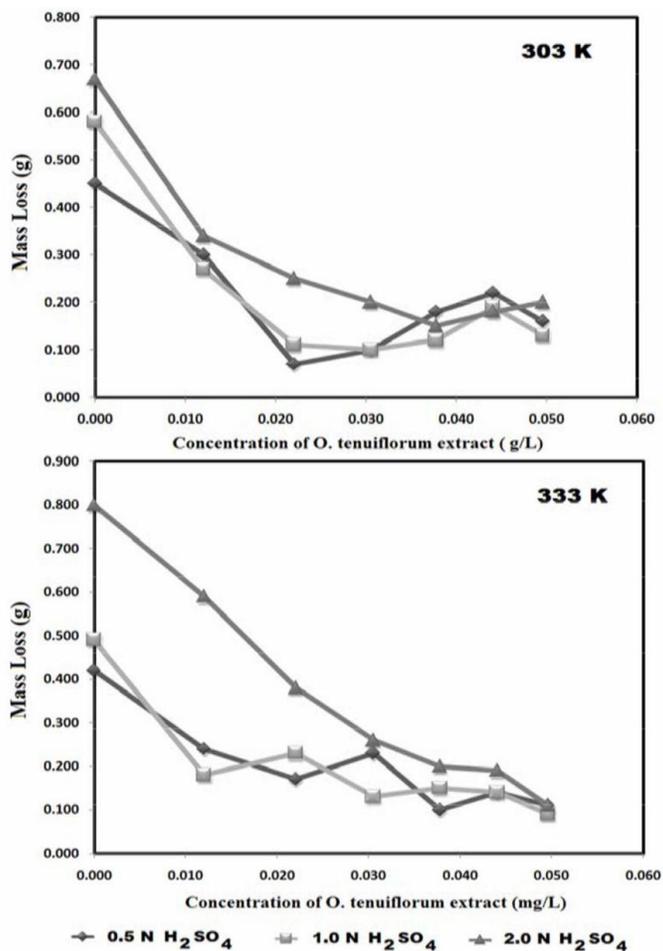


Fig.-1: Mass loss change variation with concentration of *O. tenuiflorum* extract

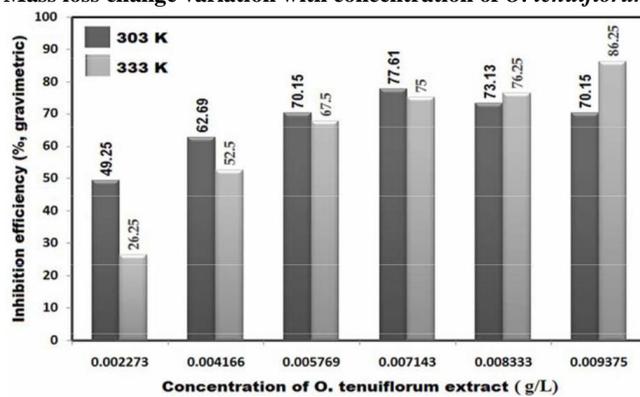


Fig.-2: Variation of inhibition efficiency

## CONCLUSIONS

It has been found that *O. tenuiflorum* leaves extract may be used as an inhibitor for zinc corrosion in H<sub>2</sub>SO<sub>4</sub> medium at 0.5N, 1.0N and 2.0N at 303K and 333K. It has also been found that the inhibitive action of *O. tenuiflorum* extract depends on temperature and concentration of the inhibitor. The present study has hence probed into the corrosion inhibition properties of *O. tenuiflorum* extract for zinc, but an in-depth analysis of the morphology of the corroded surface SEM and FTIR analyses is needed to obtain information about the adsorption mechanism of the specific inhibitor molecules on the zinc surface.

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