# INHIBITION ACTION OF LAWSONE ON THE CORROSION OF MILD STEEL IN ACIDIC MEDIA

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**Abstract:**The use of inhibitors is one of the most practical methods for protection against corrosion. Lawsone, 2-hydroxy-1,4-naphthoquinone, the main active ingredient of Henna (*Lawsonia inermis*) plant was extracted, isolated and subjected to several studies. The corrosion inhibition of lawsone on the corrosion of mild steel in 1.0 M hydrochloric acid was studied using weight loss method. It was found that lawsone acts as a good corrosion inhibitor for mild steel in 1.0 M HCl medium. The inhibition efficiency increases with increasing of lawsone concentration. The inhibitive action was addressed in view of adsorption of lawsone molecules on the metal surface. It was found that this adsorption follows Langmuir adsorption isotherm in all tested systems and the adsorption is not activated.

**Key words:** Corrosion inhibition, Hydrochloric acid, Mild steel, 2-hydroxy-1,4-napthoquinone

## Introduction

Corrosion problems have received a considerable attention because of the attack on materials. The use of inhibitors is one of the most practical methods for protection against corrosion. A corrosion inhibitor is a substance which is added in small amounts to a corrosive medium to reduce its ability for corrosion. Mild steel is an alloy of iron with carbon (carbon content 0.16-0.25%) which undergoes corrosion easily in acidic medium.The study of mild steel corrosion phenomenon has become important particularly in acidic media because of the increased industrial applications of acid solutions and also elevated levels of hydrogen ions in the atmosphere due to pollution. As an example, the refining of crude oil results in a variety of corrosive conditions. Refinery corrosion is generally caused by a strong acid attacking the equipment surface (Scattergood, 1992).The majority of well-known inhibitors are organic compounds containing heteroatoms, such as O, N or S, and multiple bonds, which allow an adsorption on the metal surface (Ali et al., 2003). These compounds can adsorb on metal surface and block the active surface sites to reduce the corrosion rate. Four types of adsorption may take place by organic molecules at metal/solution interface: (a) electrostatic attraction between the charged molecules and the charged metal, (b) interaction of uncharged electron pairs in the molecule with the metal, (c) interaction of p-electrons with the metal and (d) combination of (a) and (c) (Shorky et al., 1998).However, the stability of the inhibitor film on the metal surface depends on some physicochemical characteristics of the molecule, related to its functional groups, aromaticity, possible steric effects, electronic density of donors, type of corrosive medium, structure, charge of metal surface and nature of interaction between the p orbital of inhibitors with the d-orbital of iron (Machnikova et al., 2008).

Although many synthetic compounds show good anticorrosive action, most of them are highly toxic to both human beings and the environment. These inhibitors may cause temporary or permanent damage to organ systemssuch as kidneys or liver, or to disturb a biochemical process or an enzyme system at some sites in the body (Raja et al., 2008). The toxicity may manifest either during the synthesis of the compound or during its applications. These drawbacks lead investigations to focus on the use of naturally occurring substances in order to find low-cost and non-hazardous inhibitors. Plant extracts have become important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention.Therefore, finding of naturally occurring substances as corrosion inhibitors is a subject of great practical significance (El-Etre, 1998, 2001, 2003)

Henna is the Persian name of a shrub known as ***Lawsonia inermis Linn***. It is native to Asia and the Mediterranean coast of Africa, However, now it is spread to other parts of the world with warmer climate also. Henna leaves are harvested throughout the year, dried and ground to a fine powder for different applications including medicinal but largely as a cosmetics (Bhuvaeshwari et al., 2002). The extracted lawsone, 2-hydroxy-1,4-napthoquinone, is the main active ingredient of Henna (Thomso,1970). Two oxygen atoms are attached to the naphthalene carbons at positions 1 and 4 to form 1,4-naphthoquinone and a hydroxyl (–OH) group is present at position 2. In the present work, inhibition action of lawsone, 2-hydroxy-1,4-napthoquinone, isolated from Henna extract as a cheap, eco friendly and naturally occurring substance on corrosion behavior of mild steel in 1 M HCl has been investigated using weight loss measurements.

## Materials and Method

**Isolation of Lawsone from Henna :**Powder of dried Henna leaves (40 g) was placed in a large beaker and distilled water (2 L) was added. The suspension was stirred with a magnetic stirrer with heating up to 70 $^0$C. After 4 h, solid $NaHCO_3$ (8.4 g) was added. The suspension was filtered under gravity overnight using three large glass funnels with filter papers. The filtrate was acidified to pH 3 by adding of 0.12 M HCl. The resulting solution was extracted with diethyl ether (4 x 200 mL) .The combined ethereal phases were washed with water (3 x 50 mL) and dried over anhydrous $MgS0_4$. Ether was removed completely in a rotary evaporator to leave a reddish brown solid (760 mg) as the crude product.

The crude lawsone was purified by column chromatography, conditions: column 40 x 3 cm; stationary phase, silica gel 60; eluent ethanol-ethyl acetate (1:2 v/v). Initially fractions of 10 mL were taken and in the region of the lawsone zone the fraction size was reduced to 3 mL. The composition of all fractions was tested by TLC. The combined desired fractions contained a small amount of a less polar impurity and were recrystallized from glacial acetic acid to yield 78 mg of brown crystals. The recrystallized sample was identified as lawsone by melting point of 193-195 $^0$C (lit. 195 $^0$C) and its UV- visible spectrum.(Berger and Sicker, 2009)

**Specimen Preparation:** The mild steel sheets of 70 x 10 x 0.5 mm dimension were used for weight loss measurements. They were mechanically abraded with 200, 400, 800 and 1000 grades of emery papers. They were first washed with distilled water followed by acetone and dried using a stream of air and stored in moisture free desiccators before use.

**Solution Preparation:** 1 M HCl solution was prepared by diluting of 37 % HCl (Merck) using distilled water. The concentration of lawsone solution employed was varied from 10-500 mg $L^{-1}$ in 1.0 M hydrochloric acid.

**Weight Loss Measurements:** After weighing accurately, the specimens were immersed in test tubes which contained 50 mL 1 M HCl with and without addition of lawsone of different concentrations. After 4 h, the specimens were taken out, washed, dried and weighed accurately. Then the tests were repeated at the temperatures, 30, 35, 40 and 45 $^0$C. The inhibition efficiency (E %) of lawsone for the corrosion of mild steel was calculated using the following equation (Singh, I., Singh, M., 1987)

$E = (W_0 - W) / W_0 \times 100\%$

where $W_0$ and W are the weight loss of mild steel in the presence and absence of the inhibitor, respectively.

## Results and Discussion

The melting point of the isolated, pure 2-hydroxy-1,4-napthoquinone was in the range of 193-195 $^0$ C which is same as the literature value, 195 $^o$C (Krishnaswamy, 2003).

As it can be seen from the UV-vis spectrum of lawsone in 0.1 M HCl (Figure 1, a), absorption maximum appears at 334 nm. This spectrum of the isolated lawsone had a close resemblance with the spectrum reported in the literature (Berger and Sicker, 2009). The long tail of the band (Figure 1, a) at 334 nm that is reaching far into the visible region, is responsible for yellowish colour of lawsone. If one removes the acidic proton and measures the UV spectrum in 0.1 M NaOH, lawsone gives an orange colour solution with the spectrum band at about 453 nm (Figure 1, b),

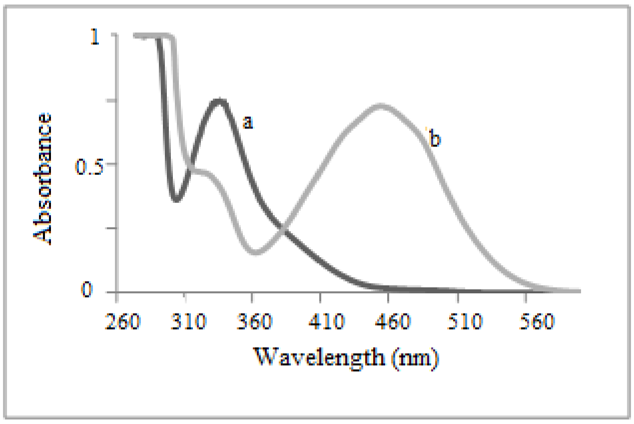



**Figure 1**. Absorption spectrum of lawsone (a) in 0.1 M HCl (b) in 0.1 M NaOH

The values of inhibition efficiencies (E) obtained from the weight loss for different concentration of lawsone in 1M HCl are given in Table 1. It is clear that inhibition efficiencies increases with increasing the inhibitor concentration.

Assuming that the corrosion inhibition was caused by the adsorption of lawsone, and the degree of surface coverage (θ) for different concentrations of lawsone in 1M HCl was evaluated from weight loss measurements using the Sekine and Hirakawa's method (Sekine ,1987).

$\theta = (W_0 - W)/(W_0 - W_m)$

where $W_m$ is the smallest weight loss.

For the value of θ (Table 1), it can be seen that the values increased with increasing lawsone concentration as a result of adsorption of more lawsone molecules on the surface of steel at high concentrations.

**Table 1**: Corrosion parameters obtained from weight loss of mild steel in 1 M HCl containing various concentrations of lawsone at different temperatures.

| Lawsone in 1M HCl (ppm) | Temperature, Inhibition efficiency (E %) and surface coverage (θ) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 30 $^0$C | | 35 $^0$C | | 40 $^0$C | | 45 $^0$C | |
| | E (%) | θ | E (%) | θ | E (%) | θ | E (%) | θ |
| 10 | 64.66 | 0.693 | 55.66 | 0.617 | 47.50 | 0.493 | 19.96 | 0.402 |
| 25 | 79.55 | 0.853 | 68.48 | 0.806 | 58.40 | 0.716 | 26.66 | 0.635 |
| 50 | 86.17 | 0.924 | 74.18 | 0.898 | 63.30 | 0.843 | 33.79 | 0.786 |
| 100 | 89.91 | 0.964 | 77.40 | 0.952 | 66.00 | 0.925 | 41.25 | 0.892 |
| 150 | 91.23 | 0.978 | 78.54 | 0.972 | 67.00 | 0.956 | 41.91 | 0.934 |
| 250 | 92.31 | 0.99 | 79.47 | 0.988 | 67.80 | 0.982 | 42.75 | 0.970 |
| 500 | 93.14 | 0.999 | 80.18 | 1.000 | 68.40 | 1.000 | 44.20 | 1.000 |

Assuming that lawsone adsorbed on the surface of mild steel forming a monolayer and ignoring the lateral interactions between the adsorbed lawsone molecules, the Langmuir adsorption isotherm was used to investigate the adsorption mechanism by the following equation (Zhao and Mu,1999)

$$c/\theta = 1/K + c$$

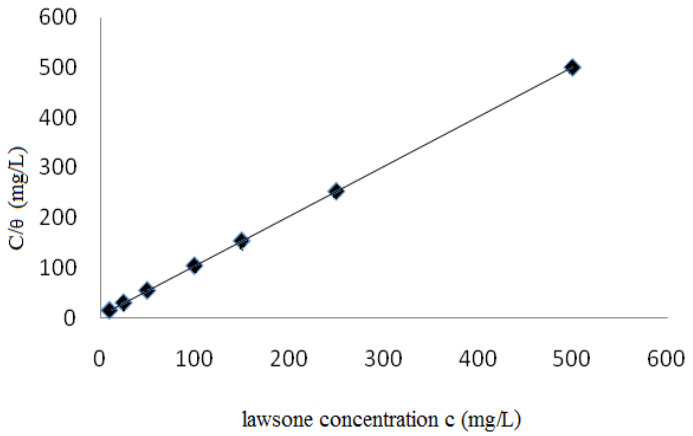


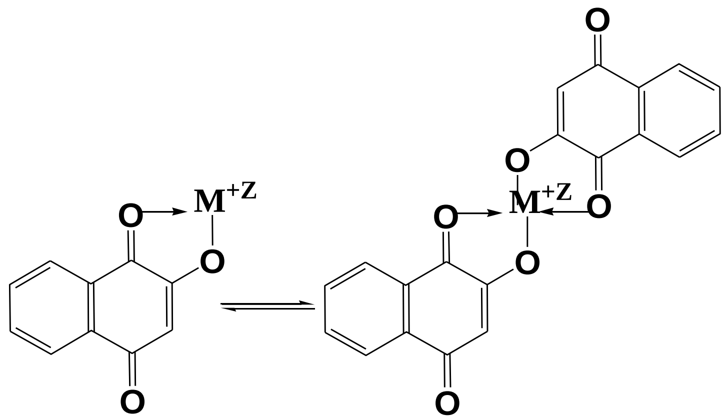

**Figure. 2**. The plot c/θ (mg $L^{-1}$) vs. c (mg $L^{-1}$) at 35 $^0$C ($R^2$ = 1.000)

Figure 2 is the relationship between c/θ and c at 35 $^0$C. The results given in the Table 2 show that linear correlation coefficient of 1.000 within the temperature range of 30 to 45 $^0$C and the slopes were 0.992,0.9870.976 and0.970. The data indicate that the assumption and the deduction were correct and at all temperatures of the experiment lawsone formed a chemical bond on the adsorption sites of mild steel surface. It could be found that the adsorption coefficient (K) decreased with increasing temperature. Lawsone gave higher values of K at lower temperatures, indicating that it was adsorbed strongly on the steel surface at lower temperatures and the adsorption process was not activated.

**Table 2**: Some parameters extracted from the linear regression between c/θ and c

| Temperature ($^0$C) | K (mg$^{-1}$ L) | Slope | Linear correlation coefficient |
|---|---|---|---|
| 30 | 0.222 | 0.992 | 1.00 |
| 35 | 0.158 | 0.987 | 1.00 |
| 40 | 0.095 | 0.976 | 1.00 |
| 45 | 0.066 | 0.970 | 1.00 |

**Mechanism of Inhibition :**Lawsone is a ligand that can chelate with various metal cations to form metal complexes. Therefore, the formation of insoluble complexes, by chelating of the metal cations with the lawsone molecules adsorbed on the metal surface, is a probable interpretation of the observed inhibition action of lawsone. The formation of metal complexes with stoichiometric ratio of 1:1 and 2:1 are shown in Figure. 2.




(a) 1 : 1 (b) 2 : 1

**Figure 3**. Forms of metal ion-lawsone complexes.

In the acidic medium, protonation of 2-hydroxy-1,4-napthoquinone takes place resulting in the rearrangement (tautomerization) as shown in the Figure 4 to give 4-hydroxy-1,2-napthoquinone. Such rearrangement, in the presence of metal cations, may enhance the complex formation ability. This could be the reason for the high inhibition efficiency in acidic media for mild steel.

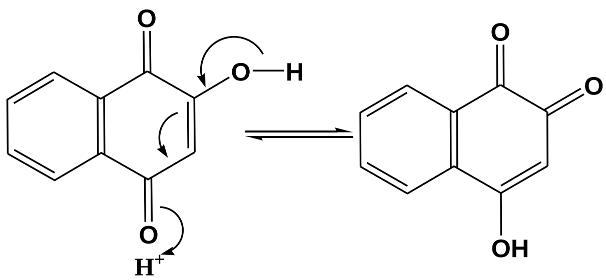



**Figure.4**. Forms of lawsone due to protonation.

## Conclusion

Lawsone was found to be an effective inhibitor for corrosion of mild steel in 1M HCl, and inhibition efficiency increased with decreasing temperature. The adsorption of lawsone on the mild steel surface from 1 M HCl obeys the Langmuir adsorption isotherm and the adsorption is not activated.

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