

## Inhibiting corrosion of carbon steel in acidic medium by using L-ascorbic acid and egypt valencia orange juice

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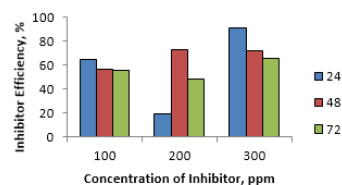
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### GRAPHICAL ABSTRACT



Inhibitor efficiency at different concentration of Egypt Valencia orange juice when reacts in 1 M CH<sub>3</sub>COOH for 24 hrs, 48 hrs and 72 hrs.

### ABSTRACT

The inhibition effect of L-ascorbic acid and Egypt Valencia orange juice on the corrosion of carbon steel in different acidic medium has been studied using weight loss method. The corrosion rate was measured after 24 hours, 48 hours and 72 hours of immersion time at different concentration of inhibitors of 100 ppm, 200 ppm and 300 ppm respectively for both inhibitors. Meanwhile, all the mediums were kept constant at 1 M for HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COOH. The experimental results obtained indicates that the inhibition effectiveness of inhibitors depend on the type of acid used as the corrosive environment, concentration of inhibitors and immersion period. The inhibition efficiency of L-ascorbic acid increases as the concentration of inhibitor increased except in HNO<sub>3</sub> and CH<sub>3</sub>COOH. On the other hand, the inhibitor efficiency for Egypt Valencia orange juice were good in all acid environment used except in HCl. The immersion period affect the inhibitor efficiency in every testing except for in CH<sub>3</sub>COOH. Inhibition of corrosion is due to the adsorption of the inhibitor at the solution interface which can be discussed in terms of specific adsorption, contact adsorption. In conclusion, Egypt Valencia orange juice serve better as effective inhibitor of the corrosion of carbon steel in acidic media compared to L-ascorbic acid. This finding might be useful to be applied as green corrosion inhibitor in sulphuric acid pickling, descaling, cleaning or any process which consumed acid, via several techniques including batch or continuous application and emulsion. However, further study need to be carry out to convert from this laboratory test to industrial application.

*Keywords:* Corrosion inhibitor; L-ascorbic acid; Orange juice; Weight loss

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## 1. INTRODUCTION

Corrosion creates serious problem in our daily lives especially in industry as it cost large amount of money. In facts, 1 tonne of steel turns into rust every 90 seconds. Corrosion manifests itself in various forms such as rusting of iron, degradation of steel, water pipelines, leaking and etc. Generally, corrosion refers to an attack on a metallic material by reaction with its surrounding. Loss of metal occurred when pure metals and alloys react chemically or electrochemically with corrosive medium to form a stable compound [1]. Hence, at the end of the reaction, the metal surface becomes corroded and yield corrosion product [1]. However, corrosion also attacks on non-metallic materials such as glass, rubber and wood. Every types of corrosion differ from each other depending on involve mechanisms that have overlapping characteristics, control initiation or propagation mechanisms.

Nowadays, use of inhibitors is one of the most practical methods to minimize corrosion. Inhibitors are added to the solution to reduce metal lost and minimize acid consumption [2]. Unfortunately, some of the inhibitors are toxic to environment [2]. Hence, scientists are trying their best to find out organic inhibitors that are environmental friendly to avoid pollutions. The most important element need to be focused in the researches on organic inhibitor, are the mechanisms of adsorption, their adsorption properties and the relationship between inhibitor structures [3]. The adsorption of inhibitors occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, triple bonds or aromatic rings [4]. As reported by many researchers, the inhibiting effect is cause by  $\pi$  electron donating effect, electron density of donating atom and also the steric effect [5].

This study is to investigate the inhibition corrosion of carbon steel in acidic medium by using L-ascorbic acid and Egypt Valencia orange juice as inhibitors. There are few methods that can be used in this study for example weight loss method, electrochemical method (polarization curves), AC-electrochemical impedance spectroscopy (IES), Scanning Electron Microscopy (SEM) analysis [14] and Fourier transform infrared (FTIR) spectroscopy [6]. However, weight loss method will be used to determine the corrosion rate in the presence and absence of inhibitors due to simple working procedure and minimal time usage to carry out this research.

## 2. EXPERIMENTAL

### 2.1 Preparation of L-ascorbic acid

For experiment containing L-ascorbic acid, concentration of L-ascorbic acid is varied at 100 ppm, 200 ppm and 300 ppm. Pure L-ascorbic acid manufactured by Merck is used in this research. 100 ppm, 200 ppm, and 300 ppm of L-ascorbic acid solution is prepared by diluting 20 mL, 40 mL and 60 mL of 500 ppm L-ascorbic acid solution in 100 mL volumetric flask respectively.

### 2.2 Preparing of Egypt Valencia orange juice

The fruits are washed under running water. Next, the orange are squeezed to obtain fresh made orange juice. The pure orange juice then is diluted by using distilled water to final concentration of 100 ppm, 200 ppm and 300 ppm in 100 mL volumetric flask. 19.2 mL, 38.2 mL and 57.4 mL of fresh made orange juice is diluted in 100 mL volumetric flask to obtain final concentration of 100 ppm, 200 ppm and 300 ppm inhibitor solution respectively.

### 2.3 Weight loss method

Weight loss measurement were performed on the carbon steel samples with a rectangular form of size (20x20x2 mm) in 1 M HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COOH solution with and without addition of different concentration of inhibitors solution. Every sample was weighed by an electronic balance and then placed in the acid solution (30mL). The duration of immersion was 24 hours, 48hours and 72 hours. After the immersion time ends, the surface of specimen was cleaned by distilled water followed by drying and the sample was weight again in order to calculate inhibition efficiency (I%) and corrosion rate (C<sub>R</sub>). The experiment was repeated for triplicates and the average value of weight loss was note.

The weight loss/cm<sup>2</sup> ΔW are given from the equation:

$$\Delta W = W_1 - W_2 / A \quad (1)$$

The efficiency, I % is given by the equation:

$$I \% = \Delta W - \Delta W_i / \Delta W \times 100 \quad (2)$$

The corrosion rate (C<sub>R</sub>) can be deduced from the equation below:

$$C_R = \frac{\Delta m}{A.t} \quad (3)$$

Where, Δ m is the mass loss (g), A is the surface area (m<sup>2</sup>), t is the immersion period (hrs) and C<sub>R</sub> is the corrosion rate of carbon steel (g m<sup>-2</sup> h<sup>-1</sup>)

## 3. RESULTS AND DISCUSSION

### 3.1 Gravimetric studies

Corrosion rates obtained from gravimetric method after several immersion times in different acidic medium are shown below. Corrosion rate differs in different types of acid. From the Table 1-4, corrosion rate is slower for Egypt Valencia orange juice in HCl, H<sub>2</sub>SO<sub>4</sub>, and CH<sub>3</sub>COOH. But for L-ascorbic acid, the corrosion rate is slightly increases in those three acids. Unfortunately, corrosion rates in HNO<sub>3</sub> for both inhibitors are quite high. However, the overall pattern of decreasing corrosion rates as the concentration of inhibitors and immersion period increases can be seen in the table below.

**Table 1** Corrosion rate of carbon steel with the presence of inhibitor in 1 M HCl for 24 hrs, 48 hrs and 72 hrs.

Inhibitor	Concentration (ppm)	Corrosion Rate (g m <sup>-2</sup> h <sup>-1</sup> )		
		24 hrs	48 hrs	72 hrs
<b>L-Asorbic acid</b>	100	6.1979	6.0833	4.3854
	200	4.4375	4.2188	0.6319
	300	0.9792	0.5417	5.8785
<b>Egypt Valencia orange juice</b>	100	0.2708	0.5625	0.3507
	200	0.4479	0.2604	0.5174
	300	0.0938	0.3906	0.2465

**Table 2** Corrosion rate of carbon steel with the presence of inhibitor in 1 M H<sub>2</sub>SO<sub>4</sub> for 24 hrs, 48 hrs and 72 hrs.

Inhibitor	Concentration (ppm)	Corrosion Rate (g m <sup>-2</sup> h <sup>-1</sup> )		
		24 hrs	48 hrs	72 hrs
L-Ascorbic acid	100	8.0833	8.1250	11.2222
	200	5.6771	8.4323	10.6389
	300	9.6979	8.1510	8.9861
Egypt Valencia orange juice	100	2.2188	1.1615	0.6944
	200	0.8542	1.2292	0.6806
	300	2.0521	1.2188	0.6424

**Table 3** Corrosion rate of carbon steel with the presence of inhibitor in 1 M HNO<sub>3</sub> for 24 hrs, 48 hrs and 72 hrs.

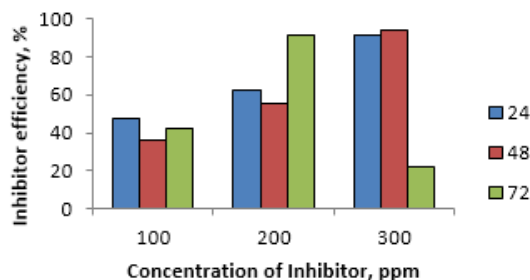
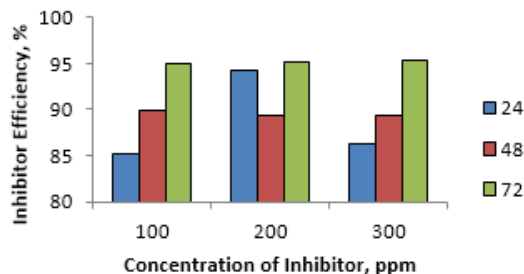
Inhibitor	Concentration (ppm)	Corrosion Rate (g m <sup>-2</sup> h <sup>-1</sup> )		
		24 hrs	48 hrs	72 hrs
L-Ascorbic acid	100	34.0000	23.2865	16.9132
	200	36.3229	27.0260	19.8924
	300	36.3958	28.8698	20.6944
Egypt Valencia orange juice	100	36.5521	26.3958	19.7431
	200	36.3333	27.1302	19.4097
	300	36.0833	26.2344	18.4444

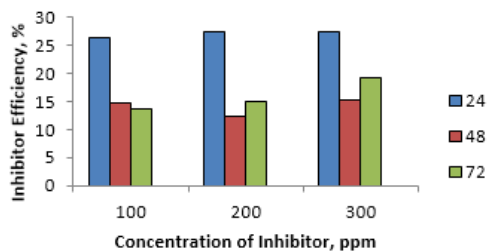
**Table 4** Corrosion rate of carbon steel with the presence of inhibitor in 1 M CH<sub>3</sub>COOH for 24 hrs, 48 hrs and 72 hrs.

Inhibitor	Concentration (ppm)	Corrosion Rate (g m <sup>-2</sup> h <sup>-1</sup> )		
		24 hrs	48 hrs	72 hrs
L-Ascorbic acid	100	1.1458	0.6563	1.2708
	200	1.4479	0.9948	1.3229
	300	2.0625	1.0260	1.1493
Egypt Valencia orange juice	100	0.7396	0.2500	0.2361
	200	1.6771	0.1563	0.2743
	300	0.1875	0.1615	0.1840

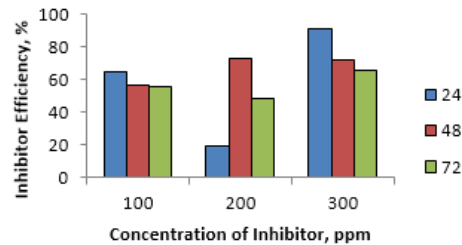
### 3.2 Inhibition efficiency measurement

Inhibition efficiency in various acid environments gives various inhibition effects. Factor of immersion of time and inhibitor concentration also contribute to effectiveness of inhibition. From the figure below, it can be seen that inhibition efficiency is higher for L-ascorbic acid in HCl but other acid solution such as HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> and CH<sub>3</sub>COOH, Egypt Valencia orange juice has higher I%.

**Fig. 1** Inhibitor efficiency at different concentration of L-ascorbic acid when reacts in 1 M HCl for 24 hrs, 48 hrs and 72 hrs**Fig. 2** Inhibitor efficiency at different concentration of Egypt Valencia orange juice when reacts in 1 M H<sub>2</sub>SO<sub>4</sub> for 24 hrs, 48 hrs and 72 hrs.



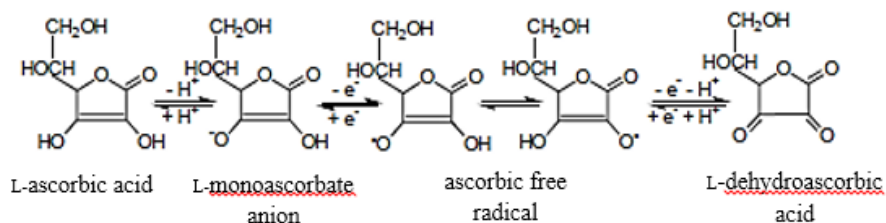
**Fig. 3** Inhibitor efficiency at different concentration of Egypt Valencia orange juice when reacts in 1 M HNO<sub>3</sub> for 24 hrs, 48 hrs and 72 hrs.



**Fig. 4** Inhibitor efficiency at different concentration of Egypt Valencia orange juice when reacts in 1 M CH<sub>3</sub>COOH for 24 hrs, 48 hrs and 72 hrs.

### 3.2 Mechanism of inhibition

L-ascorbic acid or Vitamin C contains various oxygen atom exists as -OH which is capable to act as corrosion inhibitors [7]. The inhibition process was attributed by the adsorption of L-dehydroascorbic acid (DHA) onto the electrode surface [8]. L-Monoascorbate anion is very reactive species which undergoes redox reaction to DHA. In pH 4-6, DHA presents chemical stability but it is hydrolysed to L-2,3-diketogluconic acid for pH > 7. Therefore, it is assumed that DHA is responsible for the inhibiting process to occur, although there is no evidence regarding the presence of DHA in the solution.



**Fig. 5** Oxidation of L-monoascorbate anion to DHA [8]

In citrus juice, ascorbic acid is the major vitamin presence in the solution [9]. The efficiency of organic inhibitor usually related to polar functional group with S, O or N atom presence in the molecule [10] such as thioethers, thioalcohols, thioamides, thiourea and hydrazine [11]. Thiourea, an organosulphur compound with composition SC(NH<sub>2</sub>)<sub>2</sub> was found to be in citrus fruit juice which also may be enhanced the corrosion inhibition [12]. It is not possible to consider that just a single adsorption mode that protects the metal surface due to the complexity of nature of adsorption and inhibition of the inhibitor. The adsorption might causes by the presence of  $\pi$ -electron or aromatic/heterocyclic rings.

Generally, there are two modes of adsorption are considered happens on the metal surface which is involving the adsorption of neutral molecule on the metal surface through chemisorption mechanism. The water molecule is being displaced from the metal surface and the sharing electrons between the hetero atoms and iron. Next, the inhibitor molecule is considered to absorb on the metal surface via donor-acceptor interaction between the  $\pi$ -electron of the aromatic or heterocyclic ring and vacant d-orbitals of surface iron atom. The second mode is the electrostatic interaction of protonated molecules with already adsorbed chloride ions in HCl solution. This assumption could be further confirmed by analysis using FTIR to examine the presence of active groups in the inhibitors.

## 4. CONCLUSION

In conclusion, the weight loss in mgcm<sup>-2</sup> of surface of carbon steel was determined with and without the addition of inhibitor in different types of acidic medium. Corrosion attack rapidly on metal surface especially, in highly acidic medium. Corrosion rate of free carbon steel is differs for different types of acid. Corrosion rate of carbon steel in the presence of inhibitors is depending on types of acid used and immersion times. Inhibition efficiency of Egypt Valencia orange juice is better than L-ascorbic acid. Egypt Valencia orange juice serve better as effective inhibitor of the corrosion of carbon steel in acidic media compared to L-ascorbic acid due to the presence of both S and N atom from thiourea and also vitamin C composition. This finding might be useful to be applied as green corrosion inhibitor in sulphuric acid pickling, descaling, cleaning or any process which consumed acid, via several techniques including batch or continuous application and emulsion. However, further study need to be carry out to convert from this laboratory test to industrial application.

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