

## **Red Onion skin extract-formaldehyde resin as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution**

### **ABSTRACT**

The resin formed with red onion skin extract (ROSE) and formaldehyde has been studied as a possible inhibitor for corrosion of Mild Steel in 1M HCl at 30-50°C by weight loss measurement. The corrosion rate of mild steel and the inhibition efficiencies of the resin were calculated. The studies reveal that at constant acid concentration, the resin acts as an effective inhibitor for mild steel corrosion in HCl media. Inhibition efficiency increases with increase in the concentration of the resin but decreases with an increase in temperature. The adsorption of the resin was in accordance with the Langmuir adsorption isotherm at all the temperature studied. The mechanism of physical adsorption is proposed for the inhibitory action of the resin based on observed decrease in inhibition efficiency with increase in temperature.

**Keywords:** *Resin, Inhibitor, Corrosion, Mild Steel, Langmuir adsorption isotherm.*

### **1. INTRODUCTION**

Mild steel has been extensively used under different condition in chemical and allied industries in handling alkaline, acid and salt solution [1]. Aqueous solutions of acids are among the most corrosive media [2]. The corrosion of mild steel and other metals in many industries, constructions, installations, and civil services such as electricity, water, and sewage supplies is a serious problem. In order to prevent or minimize corrosion, inhibitors are usually used especially in flow cooling systems [3]. Several inhibitors in use is either synthesized from cheap raw materials or chosen from compounds having hetero atoms in their aromatic or long chain carbon system [4].

Organic, inorganic, or a mixture of both inhibitors can inhibit corrosion by either chemisorption on the metal surface or physisorption [3]. However, in the application of these inhibitors for corrosion control, factors such as cost, toxicity, availability and environmental friendliness are very important. Thus, recently researchers are focusing on natural product as corrosion inhibitor [5, 6].

Red onion skin has been analysed and found to contain quercetin, a conjugated and electron rich compound, responsible for its inhibitory action [7]. In our present study, formaldehyde is to form a resin with quercetin, from red onion skin extract, to give a compound of higher molecular weight and yet soluble in water. The inhibitory property of this Red onion skin-formaldehyde is thus evaluated on mild steel corrosion in HCl acid solution.

### **2. MATERIALS AND METHODS**

## 2.1 Materials

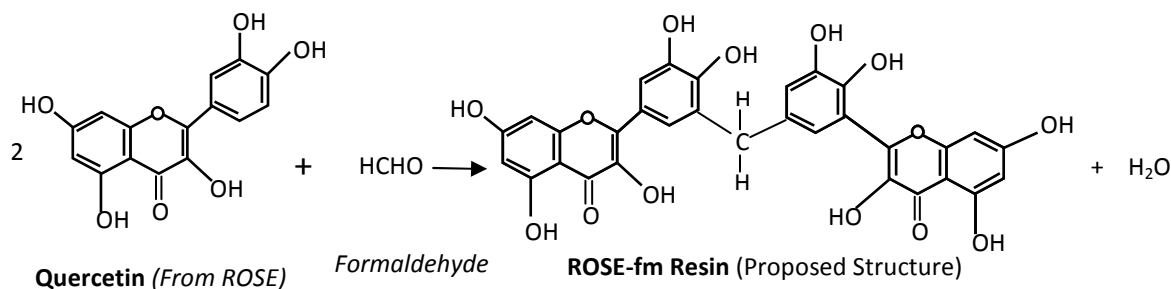
Mild steel sheets with weight percentage composition as follows: C, 0.05; Mn, 0.6; P, 0.36; Si, 0.03 were used. Each mild steel sheet, which was 0.14 cm in thickness, was mechanically pressed-cut into coupons of dimension 2cm × 4cm. These coupons were used as procured without further polishing, but were degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture-free desiccator prior to use [8].

## 2.2 Extraction of Red Onion Skin

The red onion skin was extracted using soxhlet extractor, which consists of a condenser, a reservoir and an extraction compartment that has a siphon tube and a solvent permeable thimble. 500g of red onion skin already pulverized was placed inside the thimble and 250ml of acetone placed in the reservoir. On application of heat from a heating mantle, the acetone vaporizes, condenses in the condenser and drops into the thimble to extract the red onion skin. After 6hours of extraction, the acetone was evaporated using a water bath, leaving behind the extract [20].

## 2.3 Resin Preparation

To a mixture of 6.0g of red onion skin extract and 30ml (37 percent w/v) formaldehyde solution, 20ml of (30 percent w/v) NaOH solution was added and refluxed for 2h. The resin that was formed was filtered off, washed thoroughly with distilled water, dried and stored [9].



**Fig. 1: Proposed structure of ROSE-fm Resin**

Stock solution of the resin was prepared by refluxing 4g of the resin for 3h in 500ml of 1M HCl. The solution was cooled, filtered and stored [10]. From the stock solution, inhibitor test solutions were prepared in concentrations of 10, 20, 30, 40 and 50% v/v in the respective corrodents.

## 2.4. Weight loss measurement

Tests were conducted under total immersion conditions maintained at 30, 40 and 50°C. The pre-cleaned and weighed coupons were suspended in beakers containing the test solutions using a glass rod and hook. All tests were made in aerated solutions. To determine weight loss with respect to time, the coupons were retrieved from test solutions at 24hrs interval progressively for 120hrs, scrubbed with bristle brush under running water, dried in acetone and re-weighed [11,12]. The weight loss was taken to be the difference between the weight of the coupons at a given time and its initial weight. From the weight loss data, the corrosion rates (CR) were calculated from equation (1):

$$CR = \frac{\Delta W}{At_{\infty}} \quad (1)$$

Where  $\Delta W$  is weight loss in mg,  $A$  is the specimen surface area in  $\text{cm}^2$  and  $t_{\infty}$  is the end time of each experiment in hours. From the corrosion rate, the inhibition efficiencies of the molecules (%) were determined using equation (2)

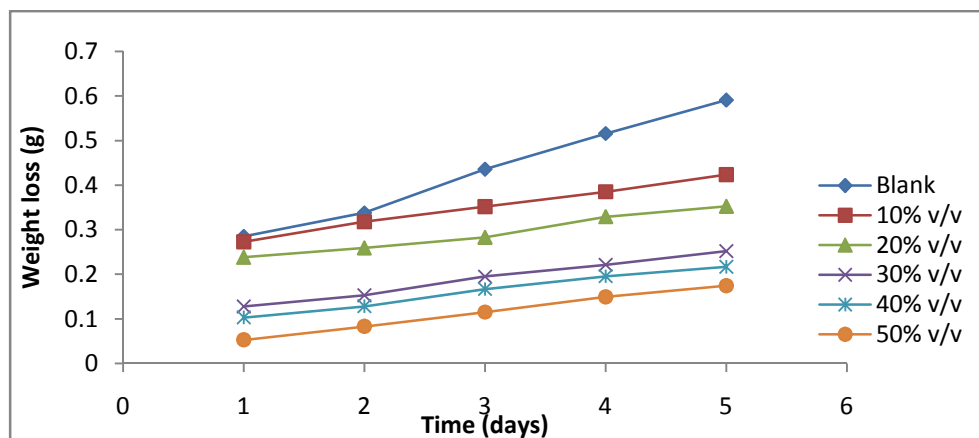
$$\%I = \left\{ \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right\} \times \frac{100}{1} \quad (2)$$

Where  $CR_{blank}$  and  $CR_{inh}$  are the corrosion rate in the absence and presence of the inhibitor respectively.

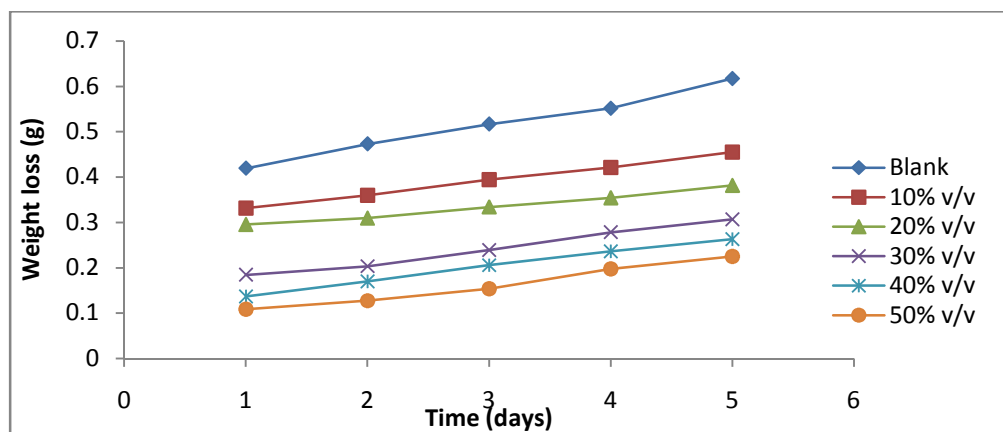
### 3. RESULTS AND DISCUSSION

#### 3.1 Effect of Concentrations of ROSE/Formaldehyde resin on the Corrosion rate of Mild Steel in 1M HCl

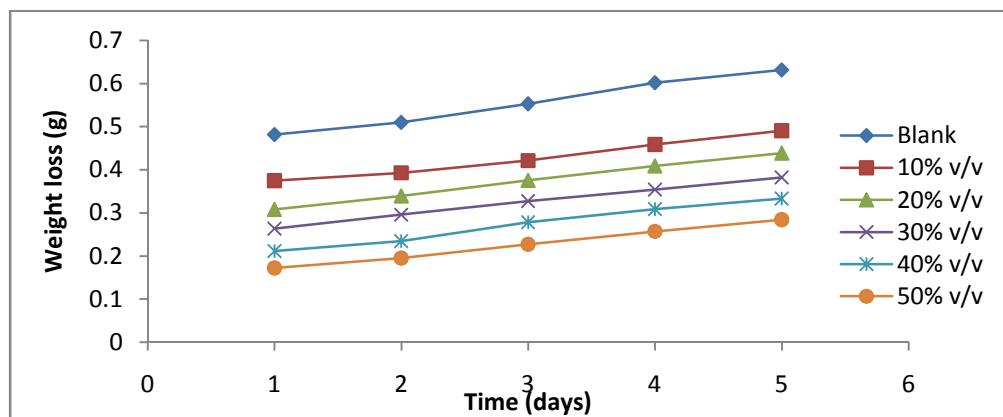
The weight loss plots of mild steel with time in 1M HCl without and with various concentrations of ROSE/formaldehyde at 30°C, 40°C and 50°C are shown in Figs 1-3. It is clear from the plots that the weight loss values of mild steel in 1M HCl solution containing ROSE/formaldehyde resin increases with exposure time and decreases as the concentration of the inhibitor increases from 10%v/v to 50%v/v at all temperatures studied, i.e. the corrosion inhibition is strengthened with the resins concentration. This trend results from the increase adsorption of organic compounds present in the ROSE/formaldehyde resin onto the mild steel surface. As a result, mild steel surfaces are effectively separated from the acid medium [13, 14]. The figures also showed that larger weight loss was obtained in the absence of the inhibitors.



**Fig 1: Variation of weight loss with time for Mild Steel in 1M HCl solution containing different concentrations of ROSE/Formaldehyde Resin at 30°C**



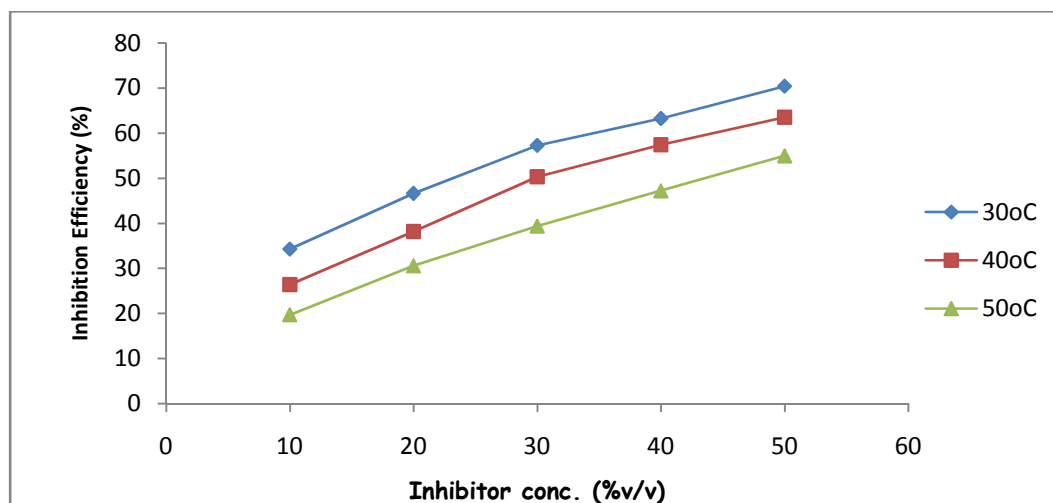
**Fig 2: Variation of weight loss with time for Mild Steel in 1M HCl solution containing different concentrations of ROSE/Formaldehyde Resin at 40°C**



**Fig 3: Variation of weight loss with time for Mild Steel in 1M HCl solution containing different concentrations of ROSE/Formaldehyde Resin at 50°C**

### 3.2 Effect of Concentration on the Inhibition Efficiency of ROSE/Formaldehyde resin on Mild Steel in 1M HCl

The plot of inhibition efficiency against inhibitor concentration of ROSE/formaldehyde resin in 1M HCl obtained from weight loss measurements are shown in Fig 4. The figure shows that inhibition efficiency increases with increase in concentration of ROSE/formaldehyde. The highest inhibition efficiency was obtained with inhibitor concentration of 50%v/v. This clearly shows that the inhibition of mild steel corrosion in 1M HCl by ROSE/formaldehyde is concentration dependent. Red onion skin extract (ROSE) have been analysed and found to contain quercetin which is responsible for its inhibitory action [15]. In addition, formaldehyde was used to form a resin with quercetin from ROSE to give a compound of higher molecular weight and yet soluble in water. The adsorption of this compound on the metal surface reduces the surface area available for corrosion. The degree of protection increases with an increase in inhibitor concentration due to higher degree of surface coverage resulting from enhanced inhibitor adsorption [16].



**Fig 4: Variation of Inhibition Efficiency with Inhibitor Concentration for Mild Steel in 1M HCl containing ROSE/Formaldehyde resin at 30, 40 and 50°C**

### 3.3 Effect of Temperature on the Corrosion rate and Inhibition Efficiency for Mild Steel in 1M HCl

To gain insight into the nature of inhibitor adsorption, the effect of temperature on the corrosion behaviour of mild steel in the presence of ROSE/formaldehyde resin was investigated. The results suggest that the resin was adsorbed on the surface of the metal at all temperatures studied. The data in Table 1 indicate that the rate of corrosion in the absence and presence of the resin increased with rise in temperature. This is because an increase in temperature usually accelerates corrosion process, particularly in media in which  $H_2$  gas evolution accompanies corrosion, giving rise to higher dissolution rates of the metal [17]. The plot in Fig 4 and the data in Table 1 show that inhibition efficiency decreases with rise in temperature for mild steel in 1M HCl. Two main types of interaction often describe adsorption of organic inhibitors on a corroding metal surface viz: chemical adsorption and physical adsorption. It has been suggested [10] that physisorbed molecules are attached to the metal at local cathodes and essentially retard dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. Analysis of the temperature dependence of inhibition efficiency gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature, suggests a chemisorption mechanism [18]. From the foregoing, the trend for ROSE/formaldehyde suggests physisorption of inhibiting species on mild steel surface in 1M HCl.

**Table 1. Calculated values of corrosion rate, inhibition efficiency and surface coverage for Mild steel coupons in 1M HCl solutions containing ROSE/Formaldehyde resin (using the weight loss technique) at 30-50°C.**

Inhibitor Conc. (%v/v)	Corrosion Rate (mg/cm <sup>2</sup> /h)			Inhibition Efficiency (I %)			Surface Coverage, $\theta$		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
Blank	14.79	15.44	18.54	-	-	-	-	-	-
10	10.59	11.37	12.68	28.43	26.39	19.69	0.2843	0.2639	0.1969
20	8.82	9.54	10.96	40.39	38.19	30.57	0.4039	0.3819	0.3057
30	6.31	7.67	9.56	57.32	50.34	39.37	0.5732	0.5034	0.3937
40	5.43	6.57	8.33	63.27	57.43	47.23	0.6327	0.5743	0.4723
50	4.37	5.63	7.11	70.44	63.53	54.98	0.7044	0.6353	0.5498

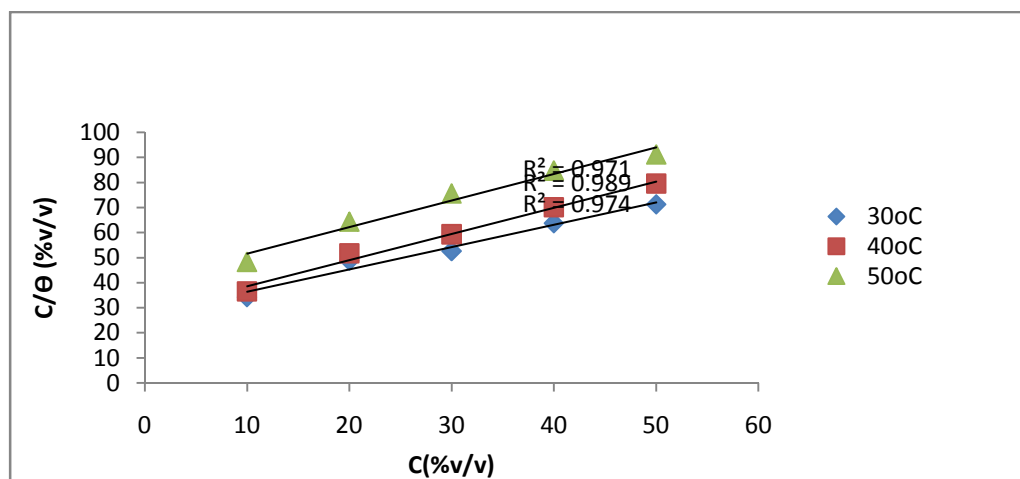
### 3.4 Adsorption considerations

Adsorption isotherms provide information about the interaction among adsorbed molecules themselves as well as their interactions with the metal surface. Surface coverage values were evaluated from the weight loss measurements assuming direct relationship between inhibition efficiency and surface coverage as follows:  $\%I = \theta \times 100$ . The surface coverage values were fitted to Langmuir adsorption isotherm.

Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

Where  $\theta$  is the surface coverage,  $C$  is the concentration,  $K_{ads}$  is the equilibrium constant of adsorption process. The plots of  $C/\theta$  against  $C$  are shown in Fig 6. Linear plots were obtained with very good correlation coefficient which seems to suggest that adsorption of the resin follow Langmuir adsorption isotherm.



**Fig 6: Langmuir Isotherm for the adsorption of ROSE/Formaldehyde resin on Mild Steel in 1M HCl at 30, 40 and 50°C**

#### 4. CONCLUSION

ROSE/Formaldehyde resin was found to be an efficient inhibitor for mild steel in 1M HCl solution, reaching about 70% at 50%v/v and temperature of 30°C. The rate of corrosion of the mild steel in 1M HCl is a function of the concentration of the resin. This rate decreased as the concentration of the resin is increased. The percentage inhibition efficiency of this inhibitor decreased as the temperature increases which indicate that physical adsorption was the predominant inhibition mechanism. ROSE/Formaldehyde resin is an eco-friendly and very cheap corrosion inhibitor for mild steel in 1M HCl solution, so it can be used to replace toxic and expensive corrosion inhibitors.

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