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Red Onion Skin Extract-formaldehyde Resin as Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

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Authors' contributions

This work was carried out in collaboration between all authors. Author OA designed the study. Author NBI performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author NBI and author AOJ managed the analyses of the study. Author NBI managed the literature searches. All authors read and approved the final manuscript.

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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 1 M 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.

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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 physiosorption [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 2 cm × 4 cm. 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. 500 g of red onion skin already pulverized was placed inside the thimble and 250 ml 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 6 hours of extraction, the acetone was evaporated using a water bath, leaving behind the extract [9].

2.3 Resin Preparation

To a mixture of 6.0 g of red onion skin extract and 30 ml (37 percent w/v) formaldehyde solution, 20 ml of (30 percent w/v) NaOH solution was added and refluxed for 2 h. The resin that was formed was filtered off, washed thoroughly with distilled water, dried and stored [10]. The proposed structure of the resin is given in Fig. 1.

Stock solution of the resin was prepared by refluxing 4 g of the resin for 3 h in 500 ml of 1 M HCl. The solution was cooled, filtered and stored [11]. 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 24 hrs interval progressively for 120 hrs, scrubbed with bristle brush under running water, dried in acetone and re-weighed [12,13]. 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):

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

Where ΔW is weight loss in mg, A is the specimen surface area in cm^2 and t_∞ is the end time of each experiment in hours. From the corrosion rate, the inhibition efficiencies of the molecules (%I) 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 1 M HCl without and with various concentrations of ROSE/formaldehyde at 30°C, 40°C and 50°C are shown in Figs. 2-4. It is clear from the plots that the weight loss values of mild steel in 1 M 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 [14,15]. The figures also showed that larger weight loss was obtained in the absence of the inhibitors.

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 1 M HCl obtained from weight loss measurements are shown in Fig. 5. 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 1 M 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 [16]. 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 [17].

3.3 Effect of Temperature on the Corrosion Rate and Inhibition Efficiency for Mild Steel in 1 M 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 [18]. The plot in Fig. 4 and the data in Table 1 show that inhibition efficiency decreases with rise in temperature for mild steel in 1 M HCl. Two main types of interaction often describe adsorption of organic inhibitors on a corroding metal surface viz: Chemical adsorption and physical adsorption. 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 a physical adsorption mechanism. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature, suggests a chemisorption mechanism [19]. From the foregoing, the trend for ROSE/formaldehyde suggests physiosorption of inhibiting species on mild steel surface in 1 M HCl.

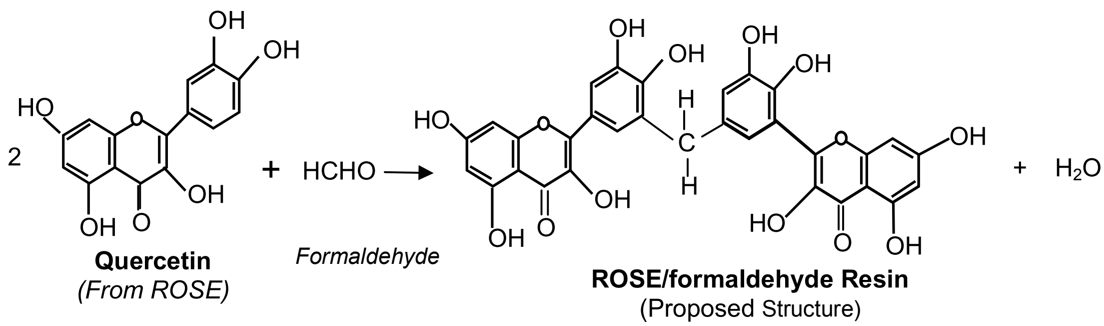

Fig. 1. Proposed structure of ROSE/formaldehyde Resin

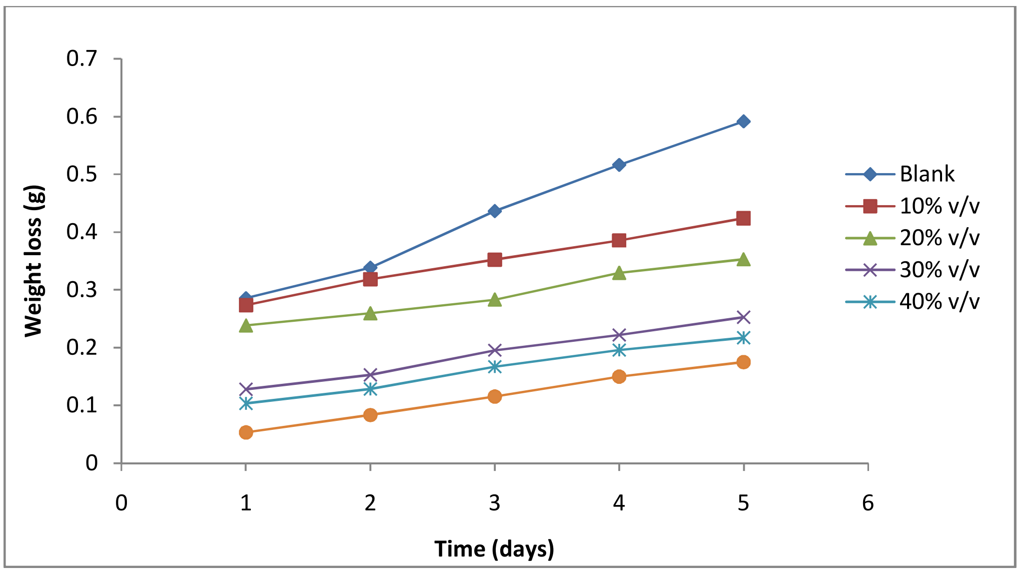

Fig. 2. Variation of weight loss with time for Mild Steel in 1 M HCl solution containing different concentrations of ROSE/Formaldehyde Resin at 30°C

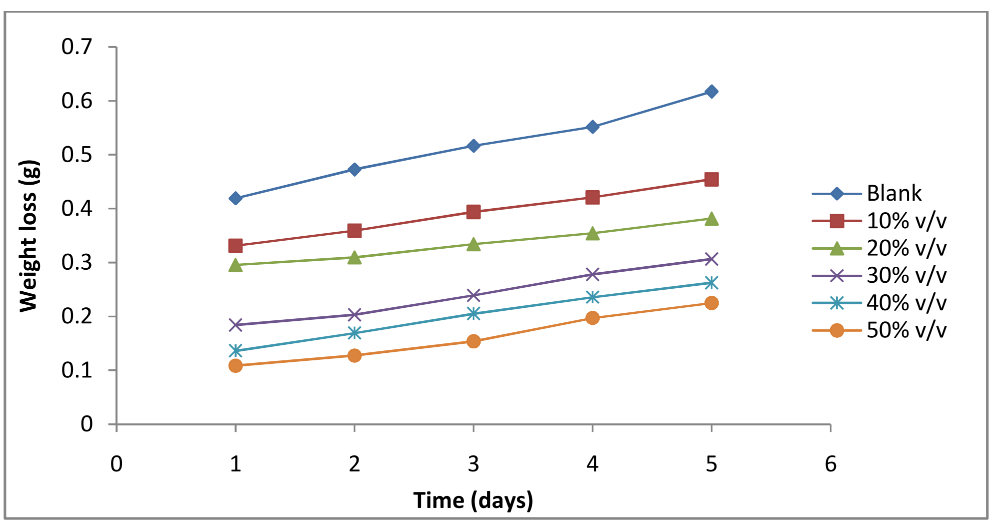

Fig. 3. Variation of weight loss with time for Mild Steel in 1 M HCl solution containing different concentrations of ROSE/Formaldehyde Resin at 40°C

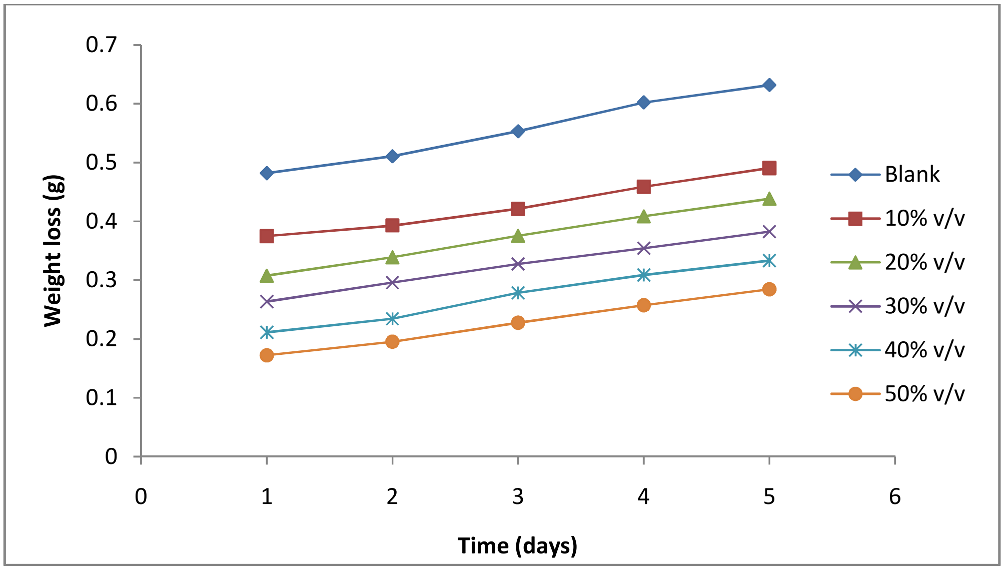

Fig. 4. Variation of weight loss with time for mild steel in 1 M HCl solution containing different concentrations of ROSE/Formaldehyde Resin at 50°C

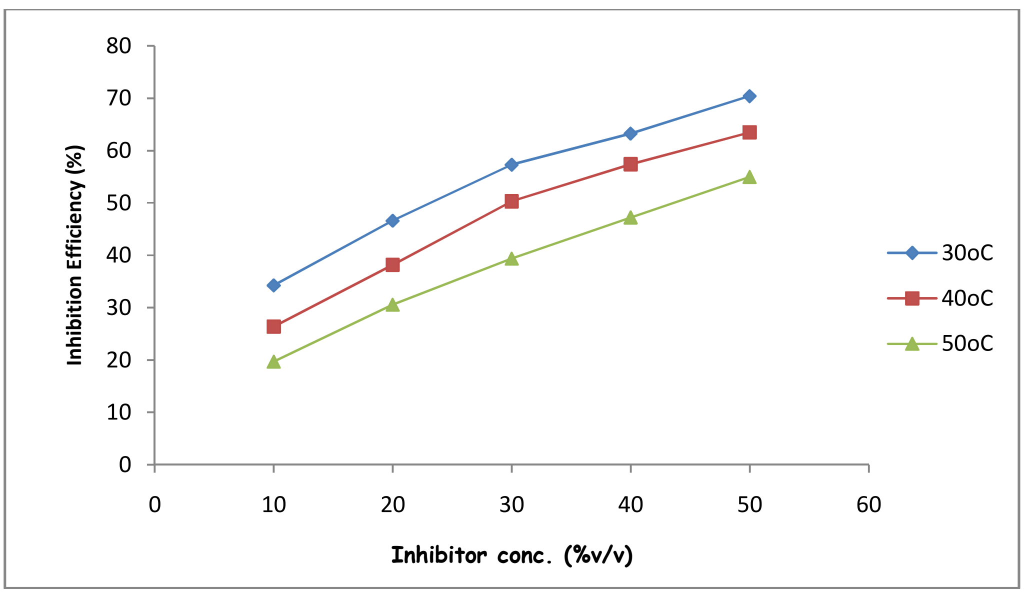

Fig. 5. Variation of inhibition efficiency with inhibitor concentration for mild steel in 1M HCl containing ROSE/Formaldehyde resin at 30, 40 and 50°C

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 = Ø × 100*. The surface coverage values were fitted to Langmuir adsorption isotherm.

Langmuir isotherm is given by the expression:

$$\frac{C}{Ø} = \frac{1}{K_{ads}} + C \qquad (3)$$

Where Ø is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process. The plots of *C/ Ø* 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.

The equilibrium constant of adsorption K_{ads} decreases with increase in temperature (Table 2), indicating that the interactions between the adsorbed molecules and the metal surface are weakened and consequently, the adsorbed molecules could become easily removable. Such data explains the decrease in the inhibition efficiency with increasing temperature [20].

The equilibrium constant of adsorption of ROSE/Formaldehyde resin on the surface of mild steel is related to the free energy of adsorption ΔG_{ads} by Equation-4.

$$\Delta G_{ads} = -2.303 \, RT \log (55.5K_{ads}) \quad (4)$$

Where *R* is the molar gas constant, *T* is the absolute temperature and 55.5 is the concentration of water in solution. The result is presented in Table 2. The negative values of ΔG_{ads} suggest that the adsorption of ROSE/Formaldehyde resin onto mild steel surface is spontaneous. The values of ΔG_{ads} obtained indicate that adsorption of ROSE/Formaldehyde resin occurs via physical adsorption mechanism. Generally, values of ΔG_{ads} less negative or equal to -20 $kJmol^{-1}$ (as obtained in this study) are consistent with electrostatic interaction between the charged metals and charged molecules which signifies physical adsorption while values more negative than -40 $kJmol^{-1}$ signify chemical adsorption [21].

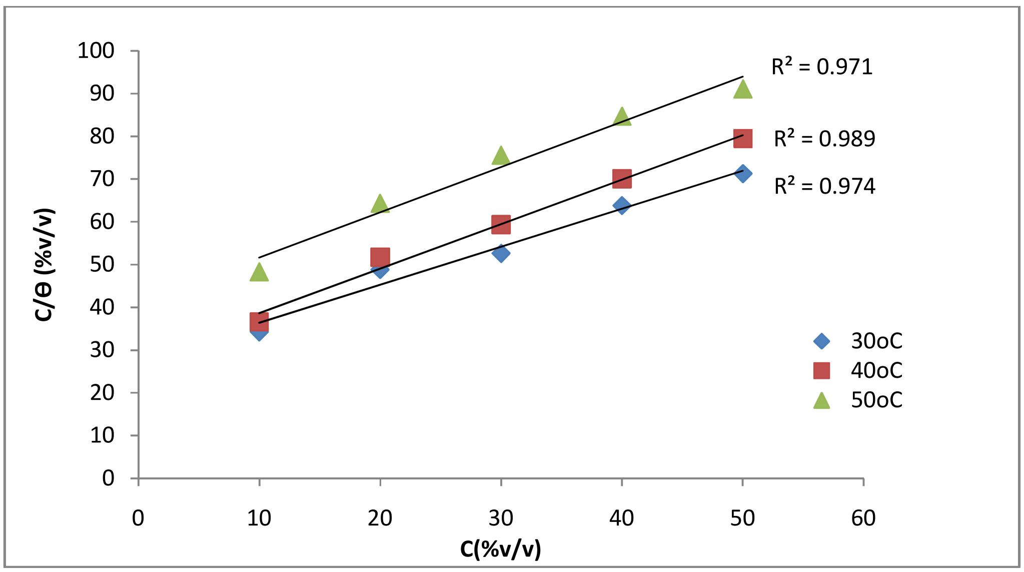

Fig 6. Langmuir Isotherm for the adsorption of ROSE/Formaldehyde resin on Mild Steel in 1 M HCl at 30, 40 and 50°C

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

Inhibitor	Corrosion rate ($mg/cm^2/h$)			Inhibition efficiency (%)			Surface coverage		
conc. (%v/v)	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

Table 2. Calculated thermodynamic parameters from Langmuir adsorption isotherm

Temperature (°C)	K_{ads} (M^{-1})	ΔG_{ads} (kJ/mol)	R^2
30	0.38	-7.68	0.9712
40	0.31	-7.41	0.9890
50	0.27	-7.27	0.9746

4. CONCLUSION

ROSE/Formaldehyde resin was found to be an efficient inhibitor for mild steel in 1 M HCl solution, reaching about 70% at 50% v/v and temperature of 30°C. The rate of corrosion of the mild steel in 1 M 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 1 M HCl solution, so it can be used to replace toxic and expensive corrosion inhibitors.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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