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Red onion skin extract-furfural resin as corrosion inhibitor for aluminium in acid medium

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ABSTRACT

The resin formed with red onion skin extract (ROSE) and furfural has been studied as a possible inhibitor for corrosion of Aluminium in 1M H_2SO_4 at 30-50^oC using the conventional weight loss technique. The studies reveal that at constant acid concentration, the resin acts as an effective inhibitor for aluminium corrosion in acidic medium. Inhibition efficiency increases with increase in the concentration of the resin but decreases with increase in temperature and immersion time. Based on the values of activation energy and the variation of inhibition efficiency with temperature, a physical adsorption mechanism is proposed for the adsorption of ROSE/Furfural resin on the surface of Aluminium. The adsorption of the resin was in accordance with the Langmuir adsorption isotherm at all the temperatures studied.

Keywords: *Resin, Red onion skin extract, Furfural, Corrosion, Aluminium, Inhibition efficiency, Langmuir adsorption isotherm.*

INTRODUCTION

Corrosion is a natural phenomenon, which can be considered either chemical or electrochemical in nature. It degrades the metallic properties of metals and make them unfit for specific role [1]. Aluminium is a soft, durable, lightweight, malleable metal with appearance ranging from silvery to dull gray, depending on the surface roughness. Aluminium and its alloy are recommended for building purpose and for various internal outfits, at various industries and highly polluted places [2]. Aluminium is remarkable for its low density and for its ability to resist corrosion to some extent due to the phenomenon of passivation [3].

The corrosion of aluminium proceeds through the following elementary reactions [4]:

$Al \rightarrow Al^{3+} + 3e^-$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (neutral / alkaline conditions)
or
$2H^+ + 2e^- \rightarrow H_2\uparrow$ (acidic conditions)

The corrosion of aluminium and its alloy in acid solutions have extensively been studied [1, 3-5]

The use of inhibitors during acid pickling procedure is one of the most practical methods for protection against corrosion in acidic media [5].

Some investigations have in recent time been made into the corrosion inhibiting properties of natural products of plant origin, which have been found to generally exhibit good inhibition efficiencies [6-10]. This area of research is of much importance because in addition to being inexpensive, readily available and renewable sources of materials, plant products are environmentally friendly and ecologically acceptable [10].

Plant products are organic in nature and some of the constituents including tannins, organic and amino acids, alkaloids and pigments are known to exhibit inhibiting action [8]**.** Red onion skin has been analysed and found to contain Quercetin, a conjugated and electron rich compound, responsible for its inhibitory action [6-7].

The present work was designed as a contribution to the growing interest on environmentally benign corrosion inhibitors. For the first time a resin is prepared and used as a corrosion inhibitor. Furfural 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.

MATERIALS AND METHODS

2.1 Materials

Aluminium sheets of the type AA1060 and purity 98.98 per cent were used. Each Al sheet of 0.1cm thickness was mechanically pressed-cut into coupons of dimensions 2cm x 4cm. The coupons were used as cut without further polishing but were, however, degreased in absolute ethanol, dried in acetone, weighed and stored in a moisture free desiccator prior to use [11].

2.2. Hydrolysis of Peanut Husk

Furfural was obtained from peanut husk by acid hydrolysis. Peanut husk powder (50g), sieved using a 60 mesh screen, and 1.5 litres of 4.5M hydrochloric acid were used for the hydrolysis. The mixture was allowed to reflux for 1hr. Thereafter, it was cooled, filtered and the filtrate containing the furfural stored in an amber coloured bottle at 28^{o}C and used up within 24hrs [12].

2.3 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.

2.4 Resin Preparation

The ROSE/furfural resin was prepared according to the method of *Akaranta et al* [12]. A mixture of 6.0g of red onion skin extract and 90ml of furfural were refluxed for 3hrs. The resin that developed was filtered off, washed free of acid and stored.

Stock solution of the resin was prepared by refluxing 4g of the resin for 3h in 500ml of 1M H_2SO_4. 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.

2.5. Weight loss measurement

Tests were conducted under total immersion conditions maintained at 30, 40 and 50^{o}C. The pre-cleaned and weighed coupons were suspended in beakers containing 150cm^3 of the test solution 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 30min interval progressively for 150mins, scrubbed with bristle brush under running water, dried in acetone and re-weighed [13, 14]. 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 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 surface coverage (θ) as a result of adsorption of inhibitor molecules, and inhibition efficiencies of the molecules (%I) were determined using equations (2) and (3), respectively.

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \quad (2)$$

$$\%I = \left\{ \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \; X \; \frac{100}{1} \right\} \quad (3)$$

Where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibiting molecules, respectively.

RESULTS AND DISCUSSION

3.1. Effect of ROSE/Furfural resin on the Corrosion of Aluminium

The corrosion and inhibition behaviour of Aluminium in 1M H_2SO_4 containing various concentrations of ROSE/Furfural resin are studied at different time (30min to150mins) and temperature (30°C, 40°C and 50°C) respectively. The weight loss of Aluminium at various concentrations of ROSE/Furfural resin, at different time in 1M H_2SO_4 is represented in Figs. 1-3.

Fig. 1: Variation of weight loss with time for Aluminium in 1M H_2SO_4 solution containing ROSE/Furfural resin at 30°C

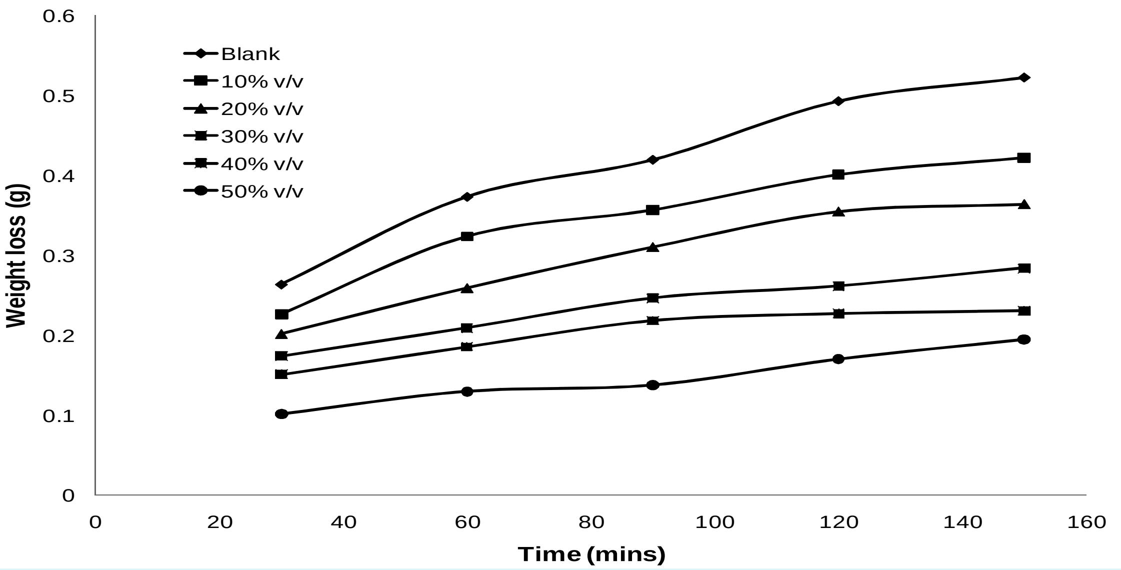


Fig. 2: Variation of weight loss with time for Aluminium in 1M H_2SO_4 solution containing ROSE/Furfural resin at 40ºC

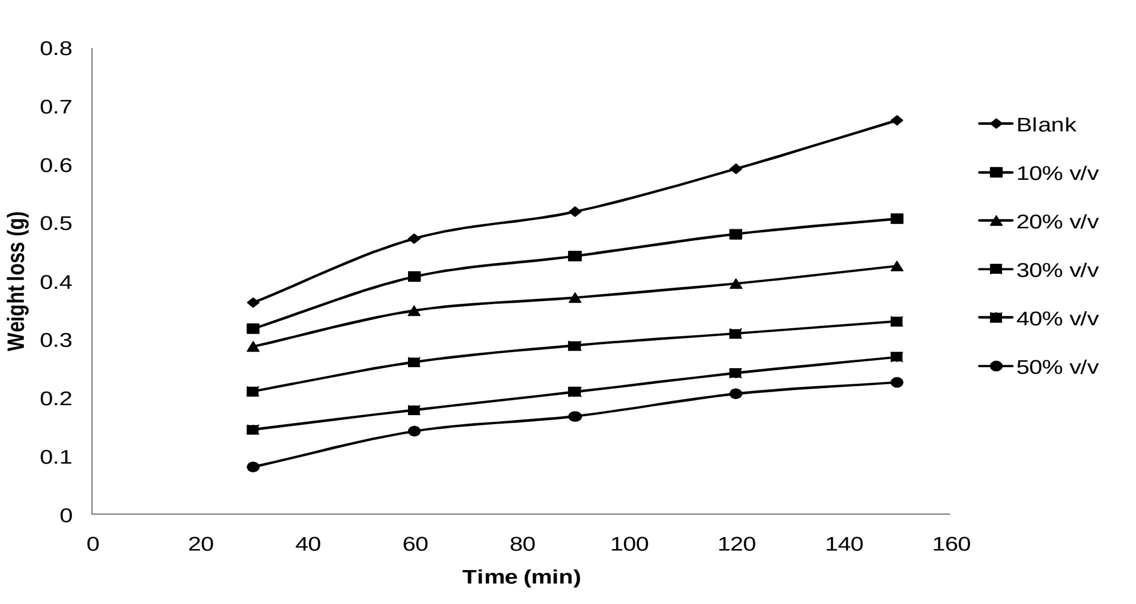
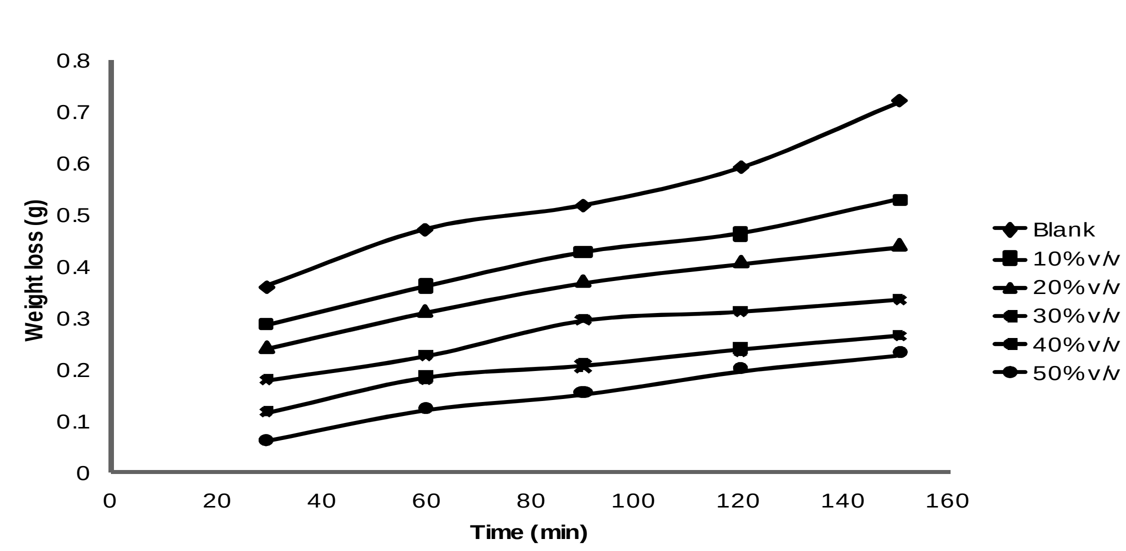


Fig. 3: Variation of weight loss with time for Aluminium in 1M H_2SO_4 solution containing ROSE/Furfural resin at 50ºC



The results show that the weight loss values increased with increase in time but decreased with increase in concentration of the resin. The decrease is due to the inhibitive effects of the resin and these effects increased with increase in the resin concentration. At 40^{o}C and 50^{o}C, as the concentration of ROSE/Furfural resin increases, the weight loss of the aluminium coupons reduce as shown by figs. 2 & 3 respectively. This shows us that ROSE/Furfural resin is still effective in inhibiting the corrosion of aluminium at these temperatures.

Table 1. Calculated values of corrosion rate, inhibition efficiency and surface coverage for Aluminium coupons in 1M H_2SO_4 solutions containing ROSE/Furfural resin (using the weight loss technique) at 30-50^{o}C.

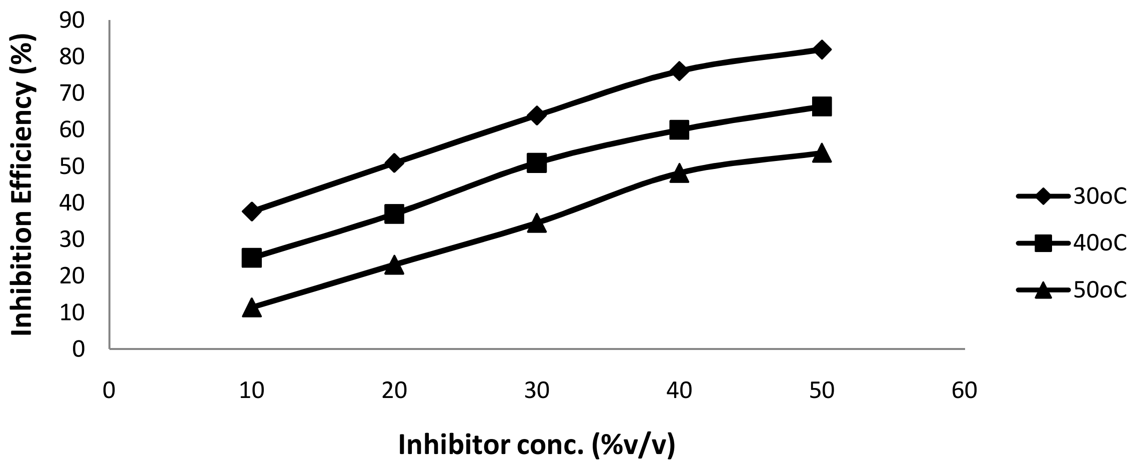
Resin Conc (%v/v)	Corrosion Rate (mg/cm^2/h)			Inhibition Efficiency (I %)			Surface Coverage, θ		
	30^{o}C	40^{o}C	50^{o}C	30^{o}C	40^{o}C	50^{o}C	30^{o}C	40^{o}C	50^{o}C
Blank	22.08	27.02	28.78	-	-	-	-	-	-
10	13.76	20.27	25.50	37.67	24.98	11.41	0.3767	0.2498	0.1141
20	10.84	17.02	22.13	50.92	37.01	23.10	0.5092	0.3701	0.2310
30	7.96	13.24	18.84	63.95	51.00	34.55	0.6395	0.5100	0.3455
40	5.28	10.81	14.91	76.10	60.00	48.20	0.7610	0.6000	0.4820
50	3.97	9.08	11.88	82.00	66.40	58.72	0.8200	0.6640	0.5872

Table 1 shows the rate of corrosion, inhibition efficiencies and surface coverage for aluminium in 1M H_2SO_4 solutions devoid of and containing different concentrations of ROSE/furfural resin. Inspection of Table 1 reveals that the corrosion rates of the aluminium decreased with increase in the resin concentration indicating that the resin inhibits the corrosion of aluminium in 1M H_2SO_4 solutions.

3.2 Effect of Temperature on the Inhibition Efficiency of ROSE/Furfural resin:

The effect of increase in temperature on the inhibition efficiency of ROSE/Furfural resin is shown graphically in Fig. 4 below.

Fig 4: Variation of Inhibition Efficiency with Inhibitor Conc. for Aluminium in 1M H_2SO_4 containing ROSE/Furfural resin at 30,40 and 50^{o}C



The resin shows a significant inhibitive effect on aluminium in H_2SO_4 solutions that reaches up to 82 % for the resin concentration of 50v/v at 30^{o}C. Fig. 4 shows the variation of inhibition efficiency with resin concentration for aluminium in 1M H$_2$SO4 solutions at different temperatures and indicates that the inhibition efficiencies increased with increase in the resin concentration and decreased with raise in temperature. The increase in inhibitive action with increase in concentration of the resin can be ascribed to the blocking of active sites of the metal surface. The active polar sites of the resin form a monolayer on the surface of aluminium. The mechanism of physical adsorption is proposed for the ROSE/Furfural resin from the trend of inhibition efficiency with temperature.

3.3 Adsorption behaviour of ROSE/Furfural resin

At any instant a fraction θ of the metal surface is covered by the inhibitor molecules and the uncovered fraction (1-θ) reacts with acid as it does in the absence of inhibitor. The surface coverage, θ values are very useful in explaining the adsorption characteristics. The surface coverage increases there by increasing the percentage inhibition. To examine the adsorption behaviour of the inhibitor, the data has been fitted to the Langmuir adsorption isotherm. A plot of log [θ/ (1-θ)] versus log C is a straight line supporting the monolayer adsorption of the inhibitor on the metal surface (Fig. 5).

Fig 5. Langmuir Isotherm for the adsorption of ROSE/Furfural resin on Aluminium in 1M H_2SO_4 at 30°C, 40°C and 50°C

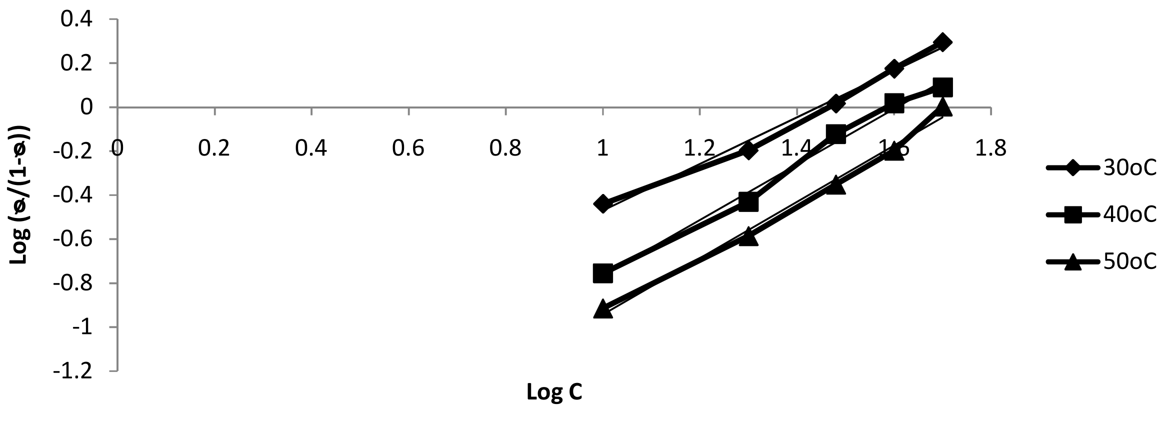


Table 2: Calculated values of Activation energy of ROSE/Furfural resin in 1M H_2SO_4 solution at 303K and 323 K

Concentration of Inhibitor (%v/v)	E_a (KJmol^{-1})
Blank	10.91
10	26.69
20	28.82
30	36.40
40	42.81
50	45.68

3.4 Activation energy

The Arrhenius equation was used to investigate the effect of temperature on the corrosion of Aluminium in the presence and absence of ROSE/Furfural resin [15].

$$CR = A\exp(-E_a/RT) \text{ -------------- } (4)$$

$$\log (CR_2/CR_1) = E_a /2.303\, R\, (1/T_1 - 1/T_2) \text{ ------------- } (5)$$

Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 (303K) and T_2 (323K) respectively. The values of Corrosion rate obtained from the weight loss measurements are substituted in Equation-4 and the calculated values of activation energy are presented in Table-2. The activation energy increased from 26.69 to 45.68 KJ/mol with increase of resin concentration. The average value of E_a obtained from the blank (10.91KJ/mol) is lower than that of the values obtained for a system containing various concentrations of ROSE/Furfural resin. This result indicated that the ROSE/Furfural resin is adsorbed on the surface of aluminium by physical adsorption.

CONCLUSION

ROSE/Furfural resin was found to be an inhibitor for aluminium corrosion in 1M H_2SO_4 solutions. The corrosion process is inhibited by the adsorption of the resin molecules on the Al surface, which promotes an increase in corrosion activation energy from 10.91KJmol^{-1} in uninhibited systems to 45.68KJmol^{-1}. The inhibition efficiency increased with increasing resin concentration but decreased with rise in temperature. The adsorption behaviour was approximated by Langmuir isotherm.

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