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Corrosion Inhibition of Mild Steel in Acid Media by Red Peanut skin extractfurfural resin

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ABSTRACT

The resin formed with red peanut skin extract (RPSE) and furfural has been studied as a possible inhibitor for corrosion of Mild Steel in 1M HCl at $30-50^{\circ}$ 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 and temperature. The adsorption of the resin was in accordance with the Langmuir adsorption isotherm at all the temperature studied. The mechanism of chemical adsorption is proposed for the inhibitory action of the resin.

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

INTRODUCTION

Mild steel is an extensively used fabrication material in sugar, petrochemical, food, paper and textile industries [1]. Mild steel corrodes easily because all common structural metals form surface oxide films when exposed to pure air but the oxide formed on mild steel is readily broken down, and in the presence of moisture, it is not repaired. Therefore, a reaction between steel (Fe), moisture (H₂O) and oxygen (O₂), takes place to form rust. This reaction is complex but it can be represented by a chemical equation of the following type:

$$4Fe + 2H_2O + 3O_2 \longrightarrow 2Fe_2O_3. H_2O \tag{1}$$

 Fe_2O_3 . H_2O is the rust, and it is not usually protective; therefore, the corrosion process is not impeded [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 chemisorptions on the metal surface or reacting with metal ions and forming a barrier-type precipitate on its surface [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 [5-8].

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Red peanut skin has been analysed and found to contain Catechin, a conjugated and electron rich compound, responsible for its inhibitory action [9]. In our present study, furfural is to form a resin with catechin, from red peanut skin extract, to give a compound of higher molecular weight and yet soluble in water.

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 $2 \text{ cm} \times 4 \text{ cm}$. 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 [10].

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°C and used up within 24hrs [11].

2.3 Extraction of Red Peanut Skin

The red peanut 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 peanut 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 peanut skin. After 6hours of extraction, the acetone was evaporated using a water bath, leaving behind the extract.

2.3 Resin Preparation

The RPSE/furfural resin was prepared according to the method of *Akaranta et al* [11]. A mixture of 6.0g of red peanut skin extract and 90ml of furfural were refluxed for 3h. 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 HCl. The solution was cooled, filtered and stored [12]. From the stock solution, inhibitor test solutions were prepared in concentrations of 10, 20, 30, 40 and 50% v/v in the respective corrodents.

2.3. 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 [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):

$$CR = \underline{\Delta W} \tag{1}$$

$$At_{\infty}$$

Where ΔW is weight loss in mg, A is the specimen surface area in cm² 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)

$$\%I = \left\{ \begin{array}{c} \frac{CR_{blank} - CR_{inh} X}{CR_{blank}} \frac{100}{1} \end{array} \right\}$$
(2)

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

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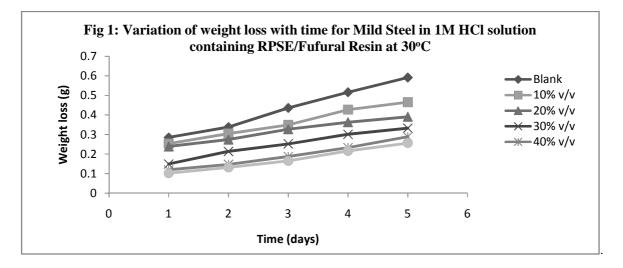
RESULTS AND DISCUSSION

3.1: Effect of Concentrations of RPSE/Furfural resin on the Corrosion rate of Mild Steel in 1M HCl

Results in Table 1 and Figs 1-3 show that corrosion rates were reduced in the presence of the resin compared to the blank acid solution. Inspection of the table and figures further reveals that corrosion rate of mild steel in the presence of the resin decreases with increase in concentration, indicating that the protection ability of the resin as inhibitor was concentration dependent. Also, corrosion rate is seen to increase with temperature rise both in the absence and in the presence of the additives. From Figures 4, it is observed that inhibition efficiency increases with increase in the concentration of RPSE/Furfural and also increases with increase in temperature. Increase in inhibition efficiency with increase in temperature is suggestive of chemical adsorption of *RPSE*/Furfural resins components onto the mild steel surface.

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

Inhibitor Conc.	Corrosion Rate (mg/cm ² /day)		Inhibition Efficiency (I %)			Surface Coverage, ∞			
(%v/v)	30°C	40°C	50°C	30°C	$40^{\circ}C$	50°C	30°C	40°C	50°C
Blank	14.79	15.44	18.54	-	-	-	-	-	-
10	11.64	11.81	11.97	21.29	23.50	29.94	0.2129	0.2350	0.2994
20	9.77	9.36	9.88	33.92	39.42	45.65	0.3392	0.3942	0.4565
30	8.31	8.12	8.49	45.53	47.42	52.55	0.4553	0.4742	0.5255
40	7.22	7.14	7.65	50.70	53.79	64.21	0.5070	0.5379	0.6421
50	6.41	5.36	6.85	56.64	65.32	77.95	0.5664	0.6532	0.7795



3.2: Effect of Temperature on the Corrosion behaviour of Mild Steel in 1M HCl in the absence and presence of the RPSE/Furfural resin

The influence of temperature on the corrosion behaviour of mild steel in 1M HCl in the absence and presence of RPSE/Furfural resin were investigated by weight loss method at 30, 40 and 50°C. In examining the effect of temperature on the corrosion inhibition process, the apparent activation energies (E_a) were calculated from the Arrhenius equation [15]:

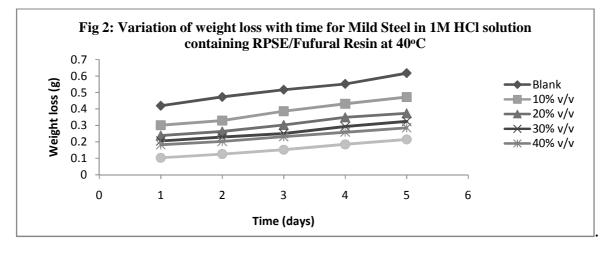
 $\log (\rho_2 / \rho_1) = E_a / 2.303 \text{ R} (1/T_1 - 1/T_2) - \dots (5)$

Where ρ_1 and ρ_2 are the corrosion rates at temperature T₁ (303K) and T₂ (323K) respectively, and R the molar gas constant. An estimate of heat of adsorption (Q_{ads}) was obtained from the trend of surface coverage with temperature as follows [12]:

 $Q_{ads} = 2.303[\log(\theta_2/(1-\Box\theta_2)) - \log(\theta_1/(1-\Box\theta_1))] \times T_1T_2/(T_2-T_1)KJmol^{-1}$

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Where θ_1 and θ_2 are the degrees of surface coverage at temperatures T_1 and T_2 . The calculated values for both parameters are given in Table 2. Increased E_a in inhibited solutions compared to the blank suggests that the inhibitor is physically adsorbed on the corroding metal surface while either unchanged or lower E_a in the presence of inhibitor suggest chemisorptions [16].



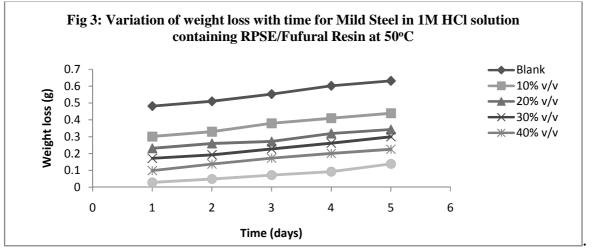
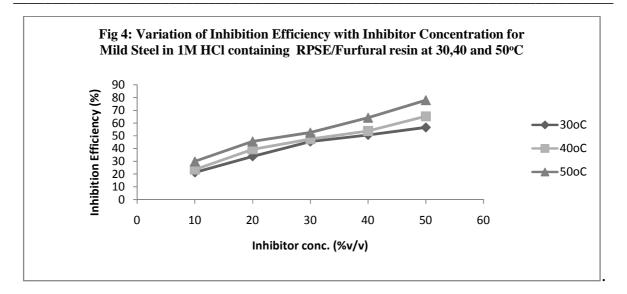
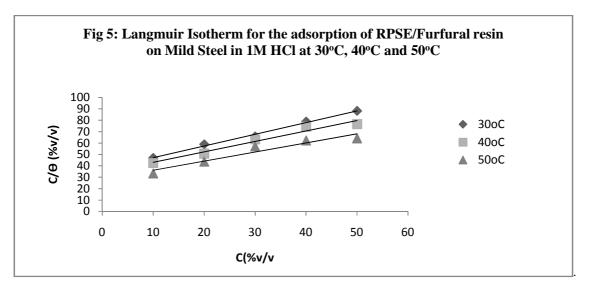


 Table 2: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for Mild Steel dissolution in 1M HCl in the absence and presence of RPSE/Furfural resin at 30- 50°C

Concentration of Inhibitor (%v/v)	E _a (KJmol ⁻¹)	Q _{ads} (KJmol ⁻¹)
Blank	9.19	-
10	6.28	6.85
20	5.93	10.22
30	5.18	19.32
40	4.63	18.90
50	3.74	21.53



It is seen from Table 2 that E_a values were lower in the presence of RPSE/Furfural compared to that in their absence. The E_a values support the earlier proposed chemisorption mechanism for RPSE/Furfural. The positive Q_{ads} values indicate that the degree of surface coverage increased with rise in temperature, supporting the earlier proposed chemisorption mechanism for RPSE/Furfural [17].



3.3Adsorption Considerations

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface. Some authors [18,19] have pointed out that adsorption on corroding surfaces never reaches the real equilibrium and tends to an adsorption steady state. However, when the corrosion rate is sufficiently small, the adsorption steady has a tendency to become quasi-equilibrium state. Therefore, it is reasonable to consider the quasi-equilibrium adsorption in a thermodynamic manner using the appropriate equilibrium isotherms. 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:

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 $\underline{C} = \underline{1} + C$

(3)

Where Θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process. The plots of C/ Θ against C are shown in Fig 5. Linear plots were obtained with very good correlation coefficient which seems to suggest that adsorption of the resin follow Langmuir adsorption isotherm.

CONCLUSION

RPSE/Furfural resin was found to be an efficient inhibitor for mild steel in 1M HCl solution, reaching about 78% at 50% v/v and temperature of 50° 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 of inhibition in the presence of this inhibitor was increased with temperature which indicates that chemical adsorption was the predominant inhibition mechanism because the quantity of adsorbed inhibitor increases with increasing temperature. RPSE/Furfural resin is an excellent, green, eco-friendly, and very cheap corrosion inhibitor for carbon steel in 1M HCl solution, so it can be used to replace toxic and highly cost chemicals.

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