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Raphia hookeri gum as a potential eco-friendly inhibitor for mild steel in sulfuric acid

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Abstract Exudate gum from *Raphia hookeri* (RH) was tested as corrosion inhibitor for mild steel in H_2SO_4 using weight loss and hydrogen evolution techniques at 30–60 °C. Results obtained revealed that RH act as corrosion inhibitor for mild steel in sulfuric acid medium. The corrosion rates in all concentrations studied increased with rise in temperature. The inhibition efficiency was observed to increase with increase in RH concentration but decreased with rise in temperature, which is suggestive of physical adsorption mechanism. The inhibitive action of RH is discussed in view of the adsorption of its phytochemical components onto steel surface, which protects the metal surface and thus do not permit the corrosion process to take place. The adsorption of the exudate gum onto the steel surface was found to follow the Langmuir adsorption isotherm. The free energies for the adsorption process and the apparent activation energies, enthalpies and entropies of the dissolution process were determined. The fundamental thermodynamic functions were used to glean important information about the RH inhibitory behavior. The results were explained in terms of chemical thermodynamics.

Introduction

Corrosion due to acids is important and expensive problem in chemical industries including the petroleum refining industry. As a result of corrosion, enormous loss is incurred due to loss of production, inefficient production, high maintenance, and the cost of corrosion control chemicals. Among the several methods devised to control metallic corrosion, the uses of inhibitors often remain the most practical and cost-effective means. Inhibitors may be regarded in general terms as a substance which when added in a small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to that environment. However, not just any chemical compound can be used as a corrosion inhibitor. There are some requirements that the compound must fulfill to do so. The chemical structure and behavior of the compound is an important consideration. In this regard, inorganic compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic compound should posses a large structure, π bond, an active center or group, etc. These features give the molecule the ability to cover a large area of a metal surface with a firmly attached film [1]. Other considerations when choosing an inhibitor include: (1) the cost of the inhibitor which can be sometimes very high when the material involved is expensive or when the amount needed is huge; (2) toxicity of the inhibitor which can cause jeopardizing effects on human beings, and other living species; (3) availability of the inhibitor, and (4) environmental friendliness.

Naturally occurring substances of both plants and animal origin otherwise tagged 'green inhibitors' are known to meet these requirements. The use of plants extracts as corrosion inhibitors have generated a lot of interest in recent times [2–7]. Among plant materials tested in our laboratory include *Dacroydes edulis* [8], *Pachylobus edulis* [9], *Vigna unguiculata* [10], and *Gum arabic* [11, 12]. The encouraging results obtained from previous investigations permit us to test more plant materials.

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The aim of this present work is to study the effect of exuduate gum from *Raphia hookeri* (RH) on the corrosion of mild steel in acidic environment at 30–60 °C using weight loss and hydrogen evolution methods. Thermodynamics is used to effectively characterize the mild steel dissolution and to properly elucidate the inhibition mechanism of the corrosion process.

Experimental details

Corrosion tests were performed on a mild steel of the following percentage composition: 0.21% C; 0.38% Si; 0.09% P; 0.01% Al; 0.05% Mn; 0.05% S, and the remainder iron. The metal was mechanically cut into coupons of dimensions 5 cm × 4 cm (total surface area = 20 cm^2). The coupons were used as cut without further polishing. However, they were degreased using absolute ethanol (BDH) dried in acetone (BDH) and stored in a dessicator devoid of moisture prior to use in corrosion studies [13, 14]. RH exudate gum was sourced locally. The exudate gum was purified following the method of Ekpe et al. [15] and reported elsewhere [8, 9]. The concentrations of inhibitor (RH) prepared and used in the study were 0.1–0.5 g/L. The concentration of H_2SO_4 (BDH) used was 0.1–1 M.

The apparatus and procedure followed for weight loss measurements were similar to that earlier reported [12–14]. Experiments were carried out under total immersion conditions in 100 mL of test solutions maintained at 30–60 °C. All tests were made in aerated solutions. The coupons were retrieved at 24 h intervals progressively for 168 h, immersed in 20% NaOH solution containing 200 g/L of zinc dust, scrubbed with bristle brush, washed, dried, and weighed [16]. The results reported are averages of triplicate determinations. The corrosion rates of mild steel in H_2SO_4 without and with different concentrations of exudate gum were calculated using the expression [17]:

$$\text{Corrosion rate (mpy)} = \frac{534W}{\rho A t}, \tag{1}$$

where W is the weight loss (gdm^{-3}), ρ the density of specimen (gcm^{-3}) (1.15 g/cm^3), A the area of specimen (cm^2), and t the exposure time (h).

From the values of corrosion rate in the presence (W_1) and absence of inhibitor (W_0), the inhibition efficiency (%I) of RH was calculated from [18]:

$$\text{Inhibition efficiency}(\%I) = \left(1 - \frac{W_0}{W_1}\right) \times 100. \tag{2}$$

The degree of surface coverage (θ) was obtained from Eq. 3

$$\text{Surface coverage}\ (\theta) = 1 - \frac{W_0}{W_1}. \tag{3}$$

Gas-volumetric experiments

The apparatus and procedure for gas-volumetric determination of corrosion rates have been described elsewhere [11, 19]. The progress of the corrosion reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. Experiments were conducted at 30–60 °C.

Results and discussion

Weight loss, corrosion rate, and inhibition efficiency

Figure 1 shows a representative plot of weight loss against time (days) for mild steel in 0.1 M H_2SO_4 solution containing no inhibitor (blank) and in the presence of different concentrations of RH exudate gum at 30 °C. Similar plots were obtained for other temperatures (40–60 °C). The figure clearly shows a reduction in weight loss of the metal coupons in the presence of different concentrations of the exudate gum compared to the free acid solution (blank).

The corrosion rates of the mild steel coupons in 0.1 M H_2SO_4 with and without different concentrations of exudate gum were determined using weight loss at 30–60 °C. The results obtained are listed in Table 1. The corrosion rate decreases with increasing concentration of the gum. This indicates that the exudate gum in the solution inhibits the corrosion of mild steel in H_2SO_4 and that the extent of corrosion inhibition depends on the amount of the extract present.

Table 1 also shows the calculated values of %I for mild steel in 0.1 M H_2SO_4 in the presence of different

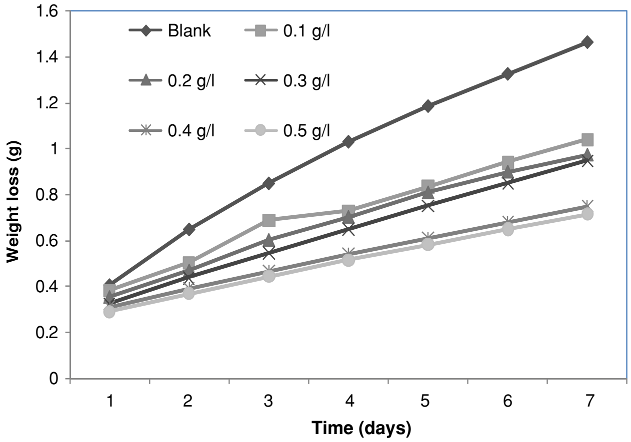

Fig. 1 A plot of weight loss against time for mild steel corrosion in 0.1 M H_2SO_4 in the absence and in the presence of different concentrations of exudate gum from RH at 30 °C

Table 1 Calculated values of corrosion rate (mpy) and %*I* for mild steel in 0.1 M H_2SO_4 in the absence and presence of various concentrations of RH at different temperatures using weight loss

Concentration (g/L)	Corrosion rate (mpy) × 10^{-3}				%*I*			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
Blank	48	57	72	76	–	–	–	–
0.1	37	39	71	75	63.1	60.2	57.4	40.8
0.2	34	35	68	73	65.2	62.4	60.5	45.2
0.3	31	33	66	67	69.1	65.2	64.2	50.0
0.4	29	30	52	51	70.8	68.5	67.0	54.1
0.5	27	29	46	49	71.9	71.1	70.3	56.5

concentrations of exudate gum at 30–60 °C from weight loss method. The %*I* was found to increase with increase in the concentration of the exudate gum. This observation is in agreement with those previously reported in H_2SO_4 [20–22]. The %*I* reached a maximum of 71.9% at 0.5 g/L exudate concentration at 30 °C. From the values of %*I*, it is clear that the corrosion inhibition may be due to the increase in the adsorption of phytochemical constituents of the exudate gum on the metal surface. The adsorption may also be due to the negatively charged metal surface and the protonated species of the constituents in the acidic solution on the metal surface [19]. Owing to the complex chemical composition of the exudate gum, it is quite difficult to assign the inhibitive effect to a particular constituent. Initial physiochemical analysis of the exudate gum identified the presence of hexuronic acid and neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and non-reducing sugars [15]. Mutual adsorptive effects of these compounds and other components present in the exudate gum cannot be ruled out in the adsorption process. The adsorption of these components on the mild steel surface reduces the surface area available for corrosion [9]. Further investigation using surface analytical techniques will enable the characterization of the active materials in the adsorbed layer and identification of the most active species.

Hydrogen evolution measurements

The spontaneous corrosion of iron can be represented by the anodic dissolution reaction:

$$Fe \rightarrow Fe^{2+} + 2e. \tag{4}$$

There must normally be a cathodic reaction to consume the electrons produced. At acidic pH, the cathodic reaction results in hydrogen evolution as follows:

$$2H^{+} + 2e \rightarrow 2H_{ads}, \tag{5}$$

$$2H_{ads} \rightarrow H_2. \tag{6}$$

H_{ads}, atomic hydrogen adsorbed on the metal surface, reacts by combining with other adsorbed H atom to form H_2 gas, which bubbles from the surface [20]. The relative rapidity and effectiveness of the gas-volumetric technique as well as its suitability for monitoring in situ, any perturbation by an inhibitor with respect to gas evolution in metal/corrodent systems have been established in earlier reports [11, 14, 23]. Figure 2 shows the plot of the volume of H_2 evolved as a function of time for mild steel corrosion in 1 M H_2SO_4 in the absence and presence of different concentrations of the inhibitor (exudate gum from RH) at 30 °C. Similar plots were obtained at 40–60 °C. The results illustrate the decrease deflection of H_2 gas evolution rate on introduction of the exudate gum into the corrodent, indicating that the exudate gum from RH actually affords corrosion inhibition of mild steel in the acidic environments.

The %*I* was calculated using Eq. 7:

$$\%I = \left(1 - \frac{V^{1}_{Ht}}{V^{0}_{Ht}}\right) \times 100, \tag{7}$$

where V^{1}_{H} is the volume of hydrogen evolved at time '*t*' for inhibited solution and V^{0}_{H} that for uninhibited solution.

Results shown in the table follow the same trend observed for weight loss measurements. %*I* increases with

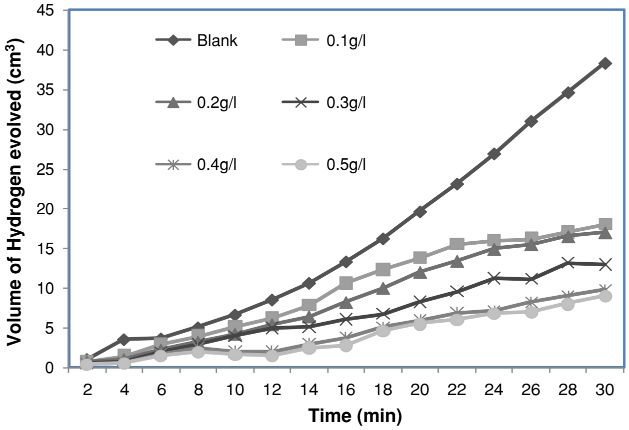

Fig. 2 A plot of volume of hydrogen evolved against time for mild steel corrosion in 0.1 M H_2SO_4 devoid and in the presence of different concentrations of exudate gum at 30 °C

Table 2 Calculated values of %*I* for mild steel in 1 M H_2SO_4 in the absence and presence of various concentrations of RH at different temperatures using hydrogen evolution method

Concentration (g/L)	%*I*			
	30 °C	40 °C	50 °C	60 °C
Blank	–	–	–	–
0.1	17.4	15.1	14.7	13.5
0.2	29.9	20.4	19.7	16.6
0.3	53.9	44.4	39.9	29.7
0.4	51.4	54.9	42.2	31.1
0.5	62.0	56.6	44.1	41.2

increase in concentration and decreases with temperature rise.

Comparison of inhibition efficiencies calculated from the weight loss and hydrogen evolution methods shows that the values of %*I* obtained from hydrogen evolution method (Table 2) are lower than that obtained from weight loss method (Table 1). This may be attributed to the difference in time required to form an adsorbed layer of the inhibitor on the metal surface that can inhibit corrosion [24].

Effects of temperature

Rodovici [25] has classified inhibitors into three groups based on the effect of temperature viz: (i) Inhibitors whose %*I* decreases with temperature increase; the value of the apparent activation energy, E_a, found is greater than that in the uninhibited solution. (ii) Inhibitors in whose %*I* does not change with temperature variation; the apparent activation energy E_a does not change with the presence or absence of inhibitors. (iii) Inhibitors in whose presence the %*I* increases with temperature increase, while the value of E_a for the process is smaller than that obtained in the uninhibited solution. Thus in examining the effect of temperature on the corrosion process in the presence of the exudates, the Arrhenius equation is helpful:

$$\log \mathrm{CR} = \frac{-E_a}{2.303RT} + \log A, \tag{8}$$

where 'CR' is the corrosion rate, E_a the apparent activation energy, R the molar gas constant, T the absolute temperature, and A is the frequency factor.

The influence of temperature on the corrosion behavior of mild steel in 0.1 M H_2SO_4 in the absence and presence of exudate gum of varying concentrations was investigated by weight loss method in the temperature range 30–60 °C during 168 h of immersion. Inhibition efficiency decreases with increase in temperature. This may be attributed to a possible shift of the adsorption–desorption equilibrium toward desorption of adsorbed inhibitor due to increased solution agitation. This, as well as the roughening of the metal surface as a result of enhanced corrosion, may also reduce the ability of the inhibitor to be adsorbed on the metal surface [20]. This result supports the idea that the adsorption of the exudate gum components onto the steel surface is physical in nature. Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency. It has been suggested that adsorption of an organic inhibitor can affect the corrosion rate by either decreasing the available reaction area (geometric blocking effect) or by modifying the activation energy of the anodic or cathodic reactions occurring in the inhibitor-free surface in the course of the inhibited corrosion process [26].

Figure 3 depicts an Arrhenius plot (corrosion rate against the reciprocal of temperature (1/*T*) for mild steel in 0.1 M H_2SO_4 solution in the absence and presence of different RH concentrations. Satisfactory straight lines of high correlation coefficients were obtained and the activation energy can be obtained from the slopes. The activation energies obtained are listed in Table 3. The apparent activation energy obtained for the corrosion process was found to be 13.2 kJ/mol. It is clear that E_a values in the presence of RH are much higher than those in the absence of RH. The higher activation energies mean a slow reaction and that the reaction rate is very sensitive to temperature. The increase in apparent activation energy in the presence of exudate gum denotes physical adsorption [27]. This conclusion is denoted by the decrease in inhibition efficiency with increasing temperature (Table 1). Similar result has been reported by El-Etre [1] on the inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves. Moreover, the increase in activation energy is proportional to the inhibitor concentration, indicating that the energy barrier for the corrosion process is also

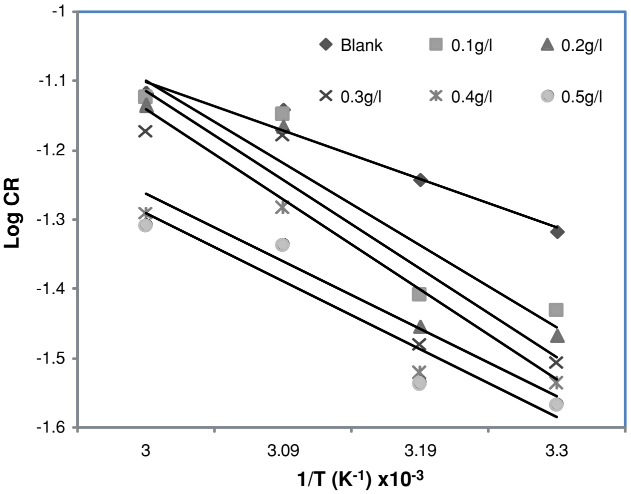

Fig. 3 Arrhenius plot for mild steel corrosion in 0.1 M H_2SO_4 in the absence and presence of various concentrations of exudate gum

Table 3 Activation parameters of mild steel in 0.1 M H_2SO_4 with and without RH exudate gum

Systems/ concentrations (g/L)	E_a (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (J/mol/K)
Blank	13.2	8.3	−26.6
0.1	22.6	19.9	−28.5
0.2	24.5	20.1	−29.3
0.3	24.9	22.4	−29.6
0.4	25.5	23.3	−33.7
0.5	26.7	24.0	−34.5

increased [28]. The increase in activation energy with inhibitor concentration is often interpreted by physical adsorption with the formation of an adsorptive film of an electrostatic character [27] (Table 3).

An alternative formulation of Arrhenius equation is [29]:

$$\mathrm{CR} = \left(\frac{RT}{Nh}\right)\exp\left(\frac{\Delta S^o}{R}\right)\exp\left(\frac{-\Delta H^o}{RT}\right), \tag{9}$$

where h is the Planck's constant, N the Avogadro's number, T the absolute temperature, R the universal gas constant, ΔS^o the entropy of activation, and ΔH^o is the enthalpy of activation. Figure 4 shows a plot of log (CR/T) as a function of 1/T. Straight lines were obtained with a slope of ($-\Delta H^o/R$) and an intercept of (ln $R/Nh + \Delta S^o/R$) from which the values of ΔH^o and ΔS^o were calculated, and listed in Table 3. From the data presented in Table 3, it seems that E_a and ΔH^o vary in the same manner. Both the activation energy and the enthalpy of activation increase as the concentration of the exudate gum increases from 0.1 g/L till it reaches 0.5 g/L of the exudate gum. This phenomenon is interpreted by the fact that at lower concentration of RH, the reduction in mild steel corrosion rate is chiefly decided by the pre-exponential factor. When the concentration is high, the decrease in steel corrosion rate is chiefly decided by the kinetic parameters of activation. These results are in agreement to those obtained in literature [30]. The positive values of ΔH^o mean that the dissolution reaction is an endothermic process and that the dissolution of steel is difficult [31]. Also, the entropy ΔS^o increases negatively with the presence of the inhibitor than the non-inhibited one. This reflects the formation of an ordered stable layer of inhibitor on the steel surface [24].

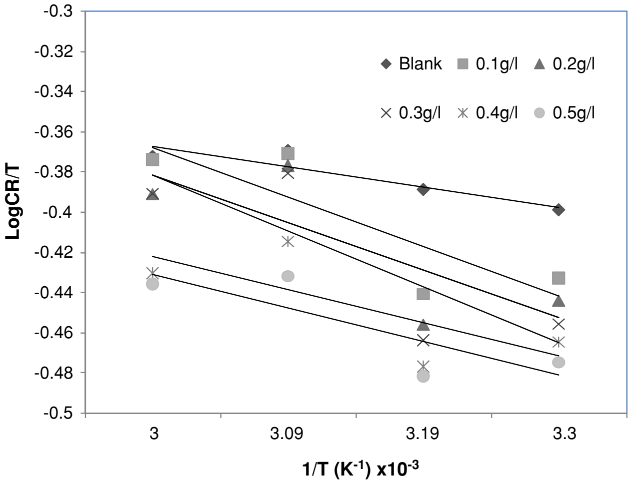

Fig. 4 Transition state plot for mild steel corrosion in 0.1 M H_2SO_4 in the absence and presence of various concentrations of exudate gum

Adsorption isotherms

It is a general assumption that the adsorption of the organic inhibitors at the metal interface is the first step in the mechanism of the inhibitors action. Organic molecules may adsorbed on the metal surface in four types: (i) electrostatic interaction between the charged molecules and the charged metal surface, (ii) interaction of unshared electron pairs in the molecule and the metal, (iii) interaction of π-electrons with the metal, and (iv) a combination of the types (i)–(iii). The values of degree of surface coverage (θ) defined as the fraction of the mild steel surface that was covered by the inhibitor and obtained directly from %I (θ = %I/100) are quite useful in determining inhibitor adsorption characteristics. Surface coverage data are applied in construction of adsorption isotherms, which give detailed information on adsorption mechanisms. Attempts were made to fit (θ) values to the Frumkin, Freundlich, Temkin, and Langmuir isotherms and correlation coefficient (R^2) values were used to determine the best-fit isotherm. By far, best result was obtained for Langmuir isotherm. The fitting to the Langmuir isotherm is shown by plotting C/θ versus C (Fig. 5) according to the equation [1, 31]:

$$\frac{C}{\theta} = \frac{1}{K_{\mathrm{ads}}} + C, \tag{10}$$

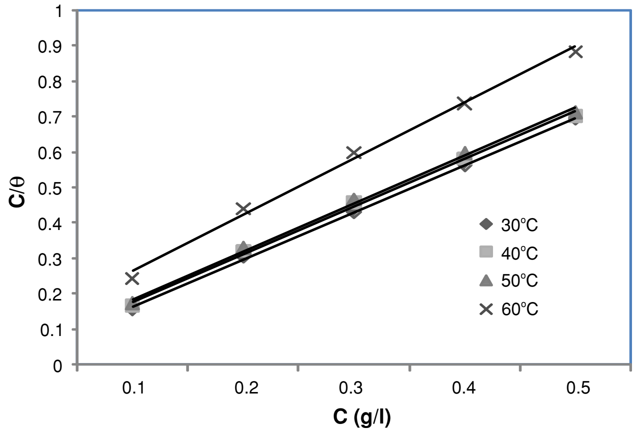

Fig. 5 The Langmuir adsorption isotherm for mild steel corrosion in 0.1 M H_2SO_4 at 30–60 °C

Table 4 Adsorption parameters for the adsorption of exudate gum from RH in 0.1 M H_2SO_4 on mild steel at different temperatures

Temperature (°C)	K_{ads}	R^2	ΔG^o_{ads} (kJ/mol)
30	32.25	0.999	−18.87
40	21.74	0.997	−18.46
50	18.51	0.996	−18.62
60	9.17	0.994	−17.25

where K_{ads} is the adsorption equilibrium constant. In this case, linear plots were obtained at different temperatures indicating that the experimental results fit the Langmuir isotherm. The isotherm postulates that there is no interaction between the adsorbed molecules and the energy of adsorption is independent on the surface coverage (θ). The values of the correlation coefficients and the adsorption equilibrium constants are listed in Table 4. The correlation coefficients are quite good and indicate that the adsorption of the inhibitor (RH) on mild steel surface follows the Langmuir adsorption isotherm. K_{ads} denotes the strength between adsorbate and adsorbent. Large values of K_{ads} imply more efficient adsorption and hence better inhibition efficiency. The values of K_{ads} decrease with increase in temperature (Table 4), suggesting that the inhibitor is physically adsorbed on the metal surface and desorption processes are enhanced by increase in temperature [23].

Free energy of adsorption can be determined with Eq. 11.

$$\Delta G^o_{ads} = -RT\ln(K \times 55.5), \tag{11}$$

where ΔG^o_{ads} is the standard free energy of adsorption and the value of 55.5 is the concentration of water in solution expressed in mol. The values of ΔG^o_{ads} obtained are listed in Table 4 and are negative in all cases. The negative values for ΔG^o_{ads} ensure the spontaneity of the adsorption on steel and that adsorption is stable in the studied temperature range. It has been reported that values up to −20 kJ/mol are characteristic for physisorption, i.e., electrostatic interaction between the charged molecules and the charged metal surface [8, 22, 23, 32].

Conclusion

1. RH exudate gum acts as inhibitor for the corrosion of steel in H_2SO_4 in the range of temperature studied.
2. The inhibition efficiency increased with increase in concentration of RH exudate gum and decreases with increase in temperature.
3. The adsorption of RH exudates gum was found to follow the Langmuir adsorption isotherm.
4. The thermodynamics/kinetics parameters obtained indicate that the adsorption of RH onto the mild steel surface is spontaneous.
5. Activation energies were higher in the presence of the exudates gum suggesting the physiosorption mechanism.

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