



## Rose (*Rosa*) extract as green corrosion inhibitor for aluminium in hydrochloric acid solution: Thermodynamic and kinetic study

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### Abstract

The inhibitive action of Rose flower extract on corrosion of aluminium in hydrochloric acid solution was investigated through weight loss, temperature effect, kinetic study and open circuit potential (OCP) methods. As inhibitor concentration increases corrosion rate decreases while percentage of inhibition efficiency (I.E.) increases. As temperature increases corrosion rate increases while I.E. decreases. Mechanism of inhibition was also investigated by calculating the thermodynamic and activation parameters like ( $\Delta G$ ), ( $Q_{ads}$ ), ( $E_a$ ), ( $\Delta H_{ads}$ ) and ( $\Delta S_{ads}$ ). It was found that the adsorption follows Langmuir adsorption isotherm. Maximum I.E. of Rose flower extract was found up to 95.60 % at 1.2 g/L inhibitor concentration in 0.75 M HCl solution. The inhibitive action of the extract is discussed in view of adsorption of rose flower molecule on the metal surface. The results obtained showed that the flower extract of Rose could serve as an effective green inhibitor for corrosion of aluminium in hydrochloric acid.

**Keywords:** corrosion, aluminium, HCl, rose flower extract, weight loss, OCP

### Introduction

Corrosion is the deterioration of materials by chemical interaction with their environment. The term corrosion is sometimes applied to the degradation of plastics, concrete and wood, but in most cases refers to metals [1-3]. Aluminum has a remarkable economic and industrial importance owing to its low cost, light weight, high thermal and electrical conductivity. It finds applications in transport sector where it is used as engine blocks, cylinder heads, and body panels, trucks and buses as sheet and plate for bodies in railway and in aircraft. In construction, aluminium (Al) is used in sheet products for roofing and wall cladding, in extrusions for windows and doors. Where as in packaging, aluminium is used in the form of alloy sheet for beverage can bodies and tops, as foil for household and commercial wrap and in manufactured packaging products such as cartons for fruit juice and packaging for pharmaceuticals. In the electrical sector, aluminium is used in the form of wire, normally reinforced with steel to form cables [4, 5]. Hydrochloric acid in the pH range of 2–4.5 is mainly used for pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing, acid descaling, chemical and electrochemical etching of aluminum and its alloys [6]. These exposures usually lead to loss of the metal due to corrosion. The protection of aluminum, aluminum alloys and its oxide films against the corrosive action of chloride ions have been extensively studied [7, 8]. The use of inhibitors for the control of corrosion of materials, which are in contact with aggressive environment, is an accepted practice. Corrosion inhibitors are substances, which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Most of organic and inorganic inhibitors are toxic to the environment implying that their use may solve corrosion problem but enhance environmental problems. So, the needs of green inhibitors or substances that have biocompatibility in nature like natural products from plant extracts. As natural products, they are a source of non-toxic, eco-friendly, bio-degradable and of potentially low costs inhibitors for preventing metal corrosion.

The name Rose comes from Latin *Rosa*. The beauty and fragrance of Rose flowers have been known since ancient times. Most Rose species are native to Asia, with smaller numbers native to Europe, Turkey, China, North America, and north western Africa [9]. Rose water is a liquid made from water and Rose petals. It is used as a perfume due to its sweet scent, but it has medicinal and culinary values, as well. Rose water can be used without any side effects, it contains numerous, powerful antioxidants. Rose water has antiseptic and antibacterial properties. Al-Turkustani [10] has studied Rose extract and Rose water as corrosion inhibitors for steel in 2 M  $H_2SO_4$  solution. Wang *et al.* [11] investigated rose extract as corrosion inhibitor for steel in 1 M HCl solution. In the present work, inhibitive action of Rose (Figure 1) extract as green inhibitor for aluminium in various concentrations of HCl solution by weight loss, kinetic, thermodynamic and OCP methods.

## Experimental

### Preparation of Specimens

The aluminium specimens with a chemical composition of 99.54 % Al, 0.090 % Si, 0.320 % Fe, 0.0012 % Cu, 0.0034 % Mn, 0.0014 % Mg, 0.0042 % Cr, 0.0046 % Ni, 0.0020 % Zn, 0.0079 % Ti, 0.0005 % Pb, and 0.0026 % Sn were used in the present study. The metal sheet, test specimens of size 5.0 x 2.50 x 0.198 cm having an effective area of 0.2797 dm<sup>2</sup> was used. The specimens were cleaned by washing with distilled water, degreased by acetone, washed once more with doubled distilled water and finally dried and weighted by using electronic balance.

### Preparation of Solution

Hydrochloric acid was used as corrosive solution having concentration of 0.75, 1.0 and 1.25 M prepared by diluting analytical grade of HCl purchased from Merck using double distilled water.

### Preparation of Rose Flower Extract

Flowers of Roses were obtained from a commercial grower in Surat, India. Impurities were removed from flowers and they were cleaned, dried in an oven at 40°C and were then ground well into powder using manual blender. From this 10 gm of the rose petal was refluxed in 100 mL distilled water for 2 hours <sup>[10]</sup>. The refluxed solution was then filtered carefully and considers this solution as stock solution. From this stock solution prepare 0.6, 0.8, 1.0, and 1.2 g/L solutions.



**Fig 1:** Rose (*Rosa*) flower

### Weight Loss Measurements

For weight loss experiment, an aluminium coupons were each suspended completely in 0.75, 1.0 and 1.25 M HCl solutions without and with 0.6, 0.8, 1.0 and 1.2 g/L concentrations of Rose flower extract with the help of glass hooks at  $301 \pm 1$  K for 24 hr (1 day). The volume of solution kept 230 mL. The coupons were retrieved after 24 hr, washed by distilled water, dried well and reweighed. From the weight loss data, corrosion rate in mg/dm<sup>2</sup>d was calculated.

### Temperature Effect

To study the effect of temperature on corrosion rate, aluminium coupons were completely immersed in 230 mL of 0.75 M HCl solution without and with different concentrations of Rose flower extract at 313, 323 and 333 K for 2 hr. From the data, inhibition efficiency (I.E.), energy of activation ( $E_a$ ) and heat of adsorption ( $Q_{ads}$ ) were calculated.

### Open Circuit Potential (OCP) Measurement

The corrosion behavior studies of metal are the measurements of OCP with time. For OCP measurement, aluminium specimens having as area of 1.0 cm<sup>2</sup> were immersed to 230 mL of 0.75 M HCl without and with of 1.2 g/L inhibitor concentration. Potential was measured immediately after the immersion of metal specimens using Ag/AgCl as a reference electrode as a function of time. The potential values were continuously recorded after each interval of 5 minutes till the potential attained a steady state value (E s.s.).

## Results and Discussion

### Weight Loss Experiments

From the weight loss data corrosion rate (C.R.) was calculated using following equation-1:

$$\text{C.R. (mg/dm}^2\text{d)} = \frac{\text{Weight loss (gm)} \times 1000}{(\text{metal surface area})\text{dm}^2 \times \text{day}} \quad (1)$$

The Inhibition efficiency (I.E.) was calculated by using the following equation-2:

$$\text{IE (\%)} = \frac{W_{\text{uninh}} - W_{\text{inh}}}{W_{\text{uninh}}} \times 100 \quad (2)$$

where,  $W_{\text{uninh}}$  = weight loss without inhibitor,  $W_{\text{inh}}$  = weight loss with inhibitor.

The degree of surface coverage ( $\theta$ ) for different concentration of the inhibitor in acidic media has been evaluated from weight loss experiments using the equation-3:

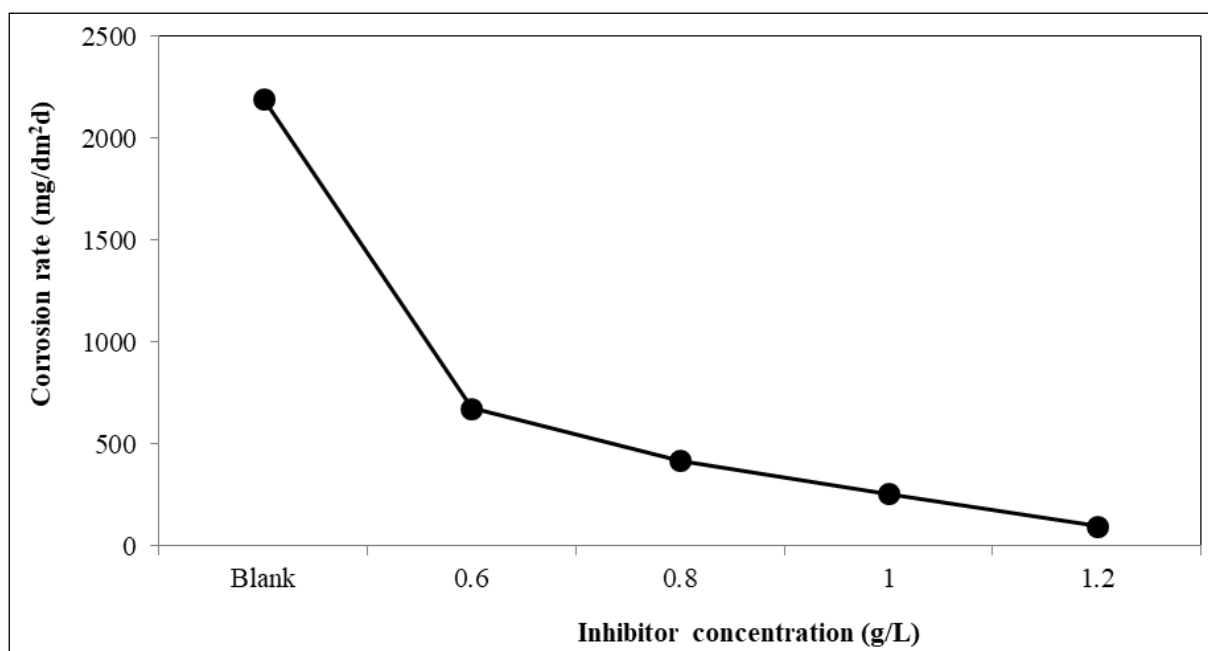
$$\theta = \frac{W_{\text{uninh}} - W_{\text{inh}}}{W_{\text{uninh}}} \quad (3)$$

**Table 1:** Corrosion rate (C.R.), Inhibition efficiency (I.E.) and Surface coverage ( $\theta$ ) of Rose flower extract on aluminium in 0.75 M HCl for an immersion period of 24 hours at  $301 \pm 1$  K.

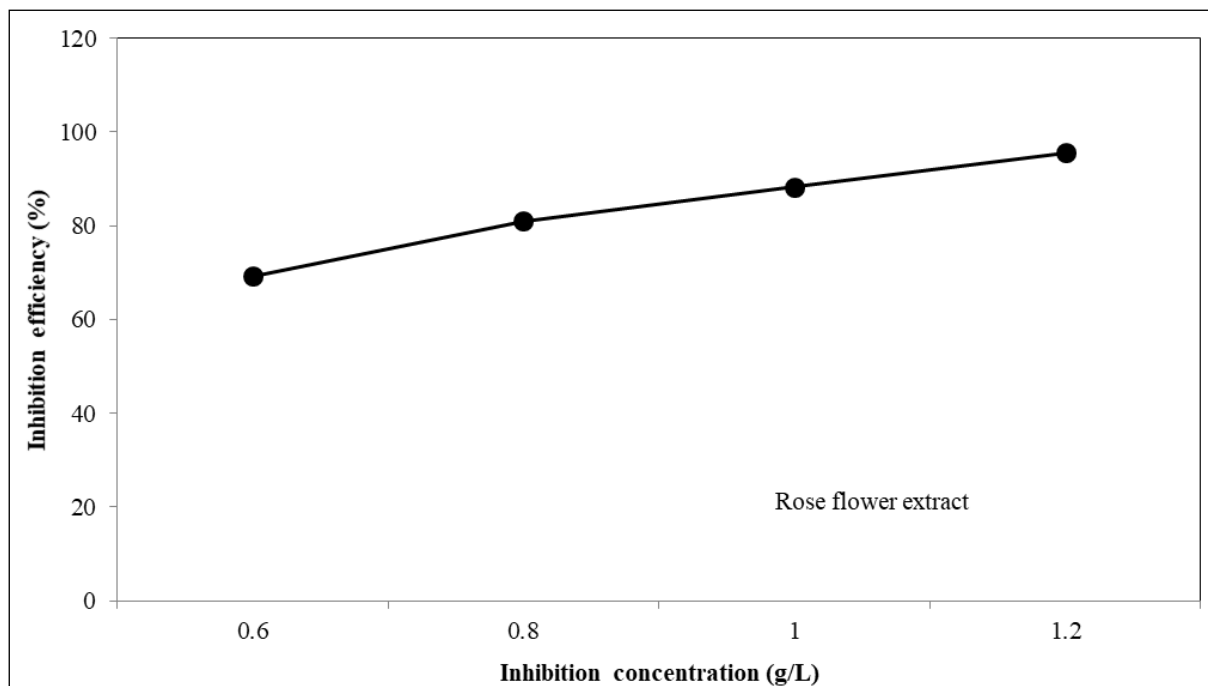
Inhibitor	Inhibitor Concentration (g/L)	CR ( $\rho$ ) (mg/dm <sup>2</sup> d)	log $\rho$	I.E. (%)	Surface coverage $\theta$	C/ $\theta$
Blank	-	2195.20	3.34	-	-	-
Rosa (Rose)	0.6	675.72	2.82	69.21	0.692	0.867
	0.8	418.30	2.62	80.94	0.809	0.988
	1.0	257.41	2.41	88.27	0.882	1.133
	1.2	96.53	1.98	95.60	0.956	1.255

### Effect of Inhibitor Concentration

At constant acid concentration, as the inhibitor concentration increases corrosion rate decreases (Figure 2) while I.E. increases (Figure 3), e.g. Rose flower extract in 0.75 M HCl solution, the I.E. found to be 69.21, 80.94, 88.27 and 95.60 % with respect to 0.6, 0.8, 1.0 and 1.2 g/L inhibitor concentrations (Table 1). The results of Table 2 and Figure 1 and 2, indicates that with increase in inhibitor concentration from 0.6 to 1.2 g/L the corrosion rate was decreased from 675.72 to 96.53 mg/dm<sup>2</sup>d.



**Fig 2:** Corrosion rate of aluminium in 0.75 M HCl solution in absence and presence of different concentration of Rose flower extract for an immersion period of 24 hours (1 day).



**Fig 3:** Inhibition efficiency (I.E.) of aluminium corrosion in 0.75 M HCl solution in presence of different concentration of Rose flower extract for an immersion period of 24 hours (1 day).

### Effect of Temperature

To investigate the influence of temperature on corrosion of aluminium in HCl, the weight loss experiments were carried out at temperature 313, 323 and 333 K in 0.75 M HCl without and with Rose flower extract for an immersion period of 2 hours. Results presented in Table 2 shows that corrosion rate increase with rise in temperature, the corrosion rate was 21451.44, 26642.76 and 43417.92 mg/dm<sup>2</sup>d corresponding to 313, 323 and 333 K respectively. Corrosion loss increases with temperature may be due to the desorption of the adsorbed molecules inhibitor and/or aggressive at higher temperature and thus exposing the fresh metal surface to further attack [12], which results in intensification of the kinetic of electrochemical reaction [13] and thus explains the higher corrosion rate at elevated temperature. The addition of Rose flower extract in corrosive media indicates that as the temperature increases I. E. decreases (Figure 4) (Table 2).

### Energy of activation (E<sub>a</sub>)

The value of energy of activation (E<sub>a</sub>) has been calculated with the help of following Arrhenius equation [14].

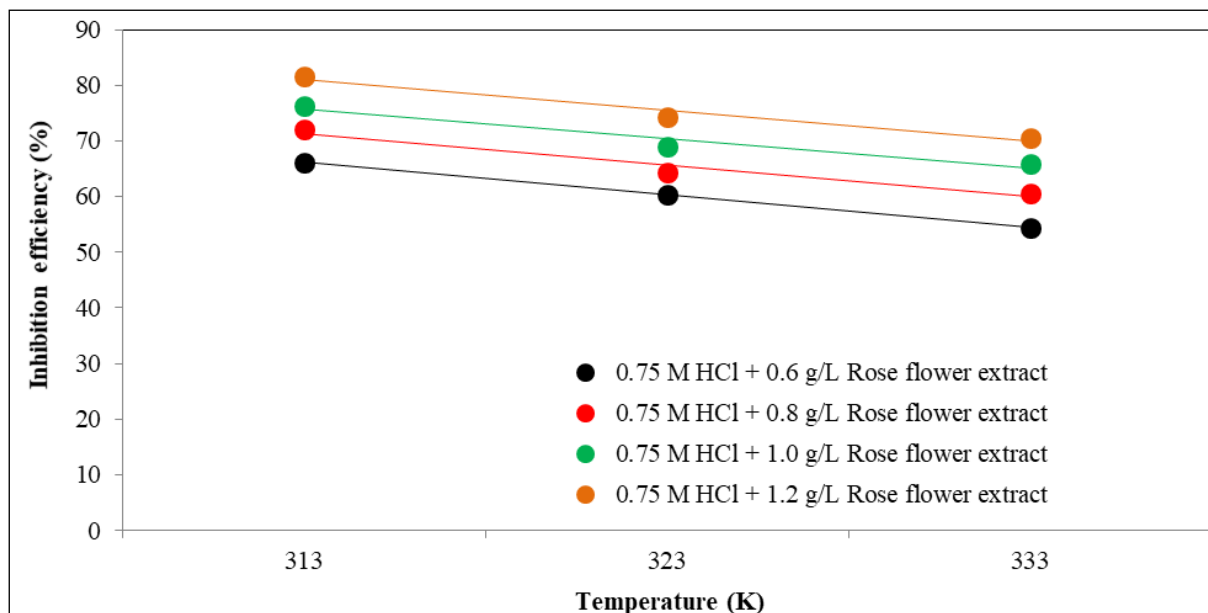
$$\log \frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

where,  $\rho_1$  and  $\rho_2$  are the corrosion rate at temperature  $T_1$  and  $T_2$  respectively.

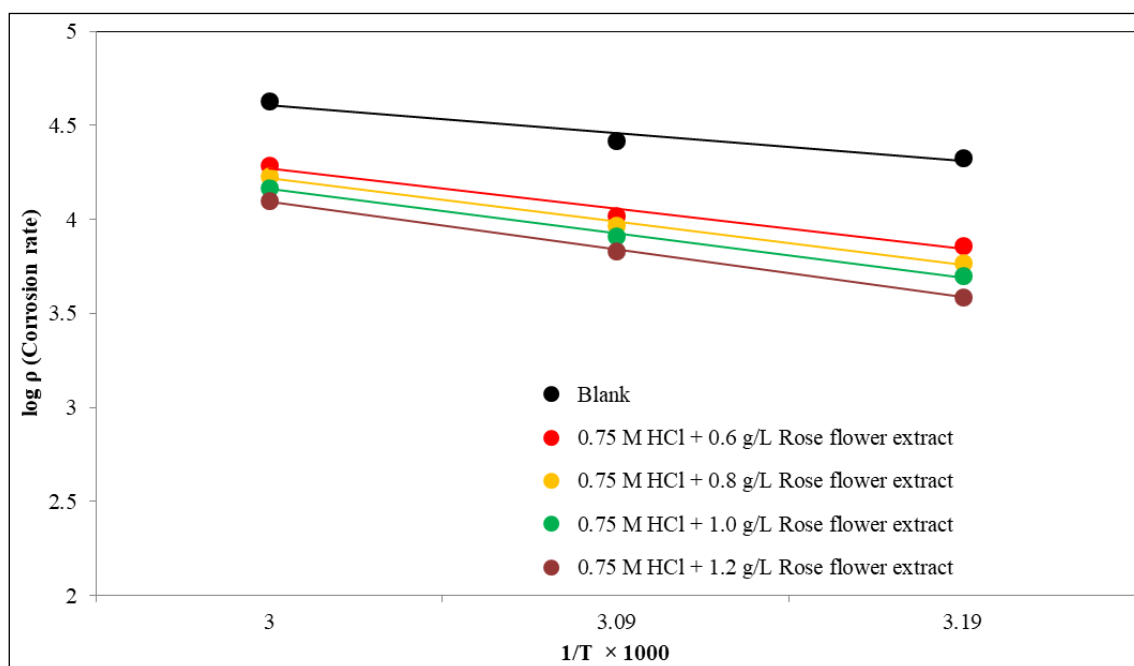
**Table 2:** Temperature effect on corrosion rate (CR), inhibition efficiency(I.E.) and activation energy (E<sub>a</sub>) for aluminium in 0.75 M HCl in absence and presence of Rose flower extract for an immersion period of 2 hours.

Inhibitor concentration. (g/L)	Temperature						Energy of activation (E <sub>a</sub> ) (kJ/mol)		
	313 K		323 K		333 K		313-323 K	323- 333 K	Mean
	CR (mg/dm <sup>2</sup> d)	I.E. (%)	CR (mg/dm <sup>2</sup> d)	I.E. (%)	CR (mg/dm <sup>2</sup> d)	I.E. (%)			
Blank	21451.44	-	26642.76	-	43417.92	-	18.21	43.64	30.92
0.6	7250.52	66.20	10554.12	60.38	19821.12	54.34	31.56	56.36	43.96
0.8	6006.36	72.00	9481.56	64.41	17118.24	60.57	38.37	52.83	45.60
1.0	5062.56	76.39	8237.28	69.08	14844.36	65.81	40.92	52.67	46.79
1.2	3947.04	81.60	6864.48	74.23	12785.04	70.55	46.52	55.62	51.07

Results given in Table 2, indicates that the values of E<sub>a</sub> were higher in inhibited acid ranging from 43.96 to 51.07 kJ/mol than E<sub>a</sub> value for uninhibited acid (30.92 kJ/mol) which indicates physical adsorption of the inhibitor on metal surface and the adsorption of inhibitor causes an increase in the E<sub>a</sub> value of the process [15]. The value of E<sub>a</sub> was also calculated from the slope of the Arrhenius plot of log p versus 1/T x 1000 (Figure 5) shows good agreement with the calculated values.



**Fig 4:** Effect of temperature on I.E. for aluminium corrosion in 0.75 M HCl at different concentration of Rose petals extract for immersion period of 2 hours.



**Fig 5:** Arrhenius plot for corrosion of aluminium in 0.75 M HCl in absence and presence of different concentration of Rose flower extract for an immersion period of 2 hours.

### Heat of adsorption ( $Q_{ads}$ )

The values of heat of adsorption ( $Q_{ads}$ ) were calculated <sup>[16]</sup> by following equation-5:

$$Q_{ads} = 2.303R \left[ \log \left( \frac{\theta_2}{1-\theta_2} \right) - \log \left( \frac{\theta_1}{1-\theta_1} \right) \right] \times \left[ \frac{T_1 T_2}{T_2 - T_1} \right] \quad (5)$$

where,  $\theta_1$  and  $\theta_2$  are the fraction of the metal surface covered by the inhibitor at temperature  $T_1$  and  $T_2$  respectively. From Table 3, it is evident that in all cases, the  $Q_{ads}$  values are negative and ranging from -13.34 to -36.27 kJ/mol. The negative values of  $Q_{ads}$  shows that the adsorption and hence the I.E. decreases with rise in temperature supporting the physisorption mechanism <sup>[17]</sup>.

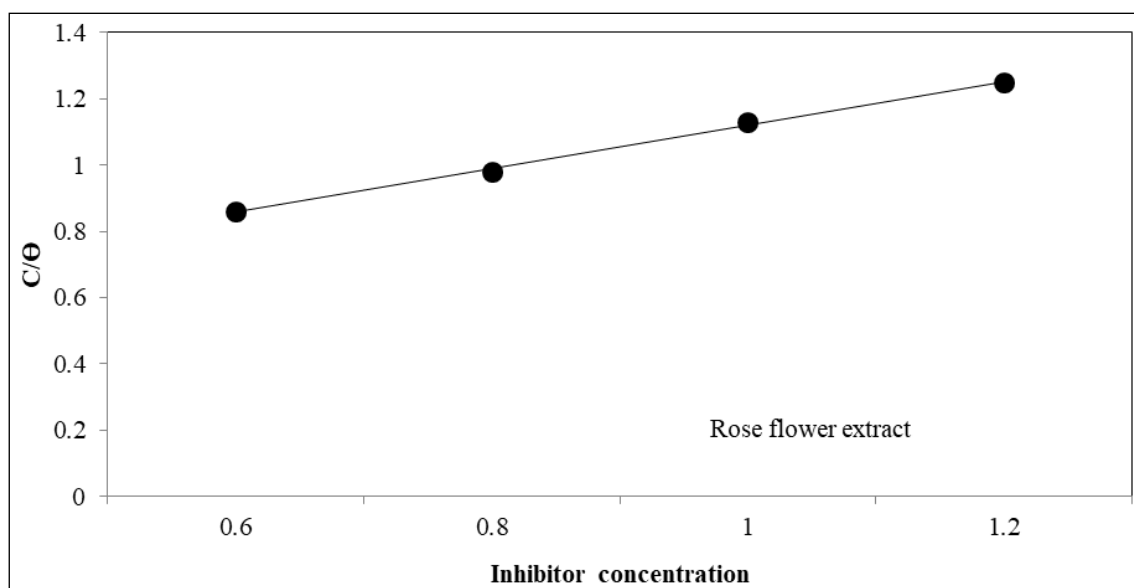
### Adsorption isotherm

Basic information on the interaction between inhibitors and a metal surface can be provided using the adsorption isotherm. In order to obtain the adsorption isotherm, the degree of surface coverage ' $\theta$ ' for different concentrations of an inhibitor in HCl solution has been evaluated. A plot of inhibitor concentration  $C_{inh}$  versus

$C_{inh}/\theta$  was presented in Figure 6 which gives straight line with slope values equal to unity indicates that the system follows Langmuir adsorption isotherm<sup>[18]</sup>. This isotherm can be represented as equation-6:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

where,  $K_{ads}$  is equilibrium constant of the adsorption process and  $C_{inh}$  is inhibitor concentration.



**Fig 6:** Langmuir adsorption isotherm plot for corrosion of aluminium in 0.75 M HCl solution containing Rose flower extract as green inhibitor at 301 K.

#### Free energy of adsorption ( $\Delta G_{ads}^{\circ}$ )

A value of  $G_{ads}^{\circ}$  was determined by the Langmuir isotherm was given by a plot of  $C/\theta$  Vs  $C$  (Figure 6). From the intercepts of the straight lines on the  $C/\theta$  axis,  $K_{ads}$  can be calculated. These values of  $K_{ads}$  are also related to the standard free energy of adsorption  $\Delta G_{ads}^{\circ}$ , as given by following equation<sup>[19, 20]</sup>.

$$\Delta G_{ads}^{\circ} = -RT \ln (55.5 K_{ads}) \quad (7)$$

where,  $R$  is the gas constant,  $T$  is the absolute temperature (K) and the value 55.5 in the above equation is the concentration of water in solution in Molar<sup>[21]</sup>,  $K_{ads}$  is the equilibrium constant of the adsorption/desorption process. The mean  $\Delta G_{ads}^{\circ}$  values were found (-06.78 kJ/mol) negative indicates that the adsorption mechanism of Rose flower extract on aluminium in 0.75 M HCl at the studied temperatures is physisorption with adsorptive layer having electrostatic character<sup>[22]</sup>. This is concluded on the fact that the values of  $\Delta G_{ads}^{\circ}$  -20 kJ/mol are consistent with physisorption, while those around -40 kJ/mol or higher are associated with chemisorption<sup>[23]</sup>.

#### Enthalpy of Adsorption ( $\Delta H_a^{\circ}$ ) and Entropy of Adsorption ( $\Delta S_a^{\circ}$ )

The enthalpy of adsorption ( $\Delta H_a^{\circ}$ ) and entropy of adsorption ( $\Delta S_a^{\circ}$ ) were calculated using the equations -8 and 9.

$$\Delta H_a^{\circ} = E_a - RT \quad (8)$$

$$\Delta S_a^{\circ} = \Delta H_a^{\circ} - \Delta G_{ads}^{\circ} / T \quad (9)$$

**Table 3:** Thermodynamic of parameters for Al in 0.75 M HCl in the absence and presence of different concentration of Rose flower extract for an immersion period of 2 hours.

Inhibitor concentration (g/L)	$Q_{ads}$ (kJ/mol)		$\Delta G_{ads}^{\circ}$ (kJ/mol)			$\Delta H_a^{\circ}$ (kJ/mol)		$\Delta S_a^{\circ}$ (J/mol K)	
	313-323 K	323-333 K	313 K	323 K	333 K	313 K	323 K	313 K	323 K
Blank	-	-	-	-	-	18.18	43.61	-	-
0.6	-21.09	-22.10	-06.57	-06.78	-06.99	28.95	53.67	0.11	0.18
0.8	-29.51	-14.66				35.76	50.14	0.13	0.18
1.0	-31.12	-13.34				38.31	49.98	0.14	0.17
1.2	-36.27	-16.47				43.91	52.93	0.16	0.18

The results revealed from Table 3 shows that  $\Delta H_a^\circ$  values were positive and increase in presence of inhibitor indicating a higher degree of surface coverage and higher protection efficiency attained due to raising the energy barrier for the corrosion reaction to occur. The enthalpy change  $\Delta H_a^\circ$  was positive and ranging between 28.95 to 53.67 kJ/mol indicating the endothermic nature of the reaction suggests that higher temperature favours the corrosion process [24]. Positive value of  $\Delta S_a^\circ$  lie between 0.11 to 0.18 J/mol K indicates the affinity of the adsorbent for the inhibitor and the corrosion process is entropically favorable [25].

#### Kinetic parameters: Rate constant (k) and Half-life ( $t_{1/2}$ )

The values of half-life ( $t_{1/2}$ ) were calculated by using the following equation [26];

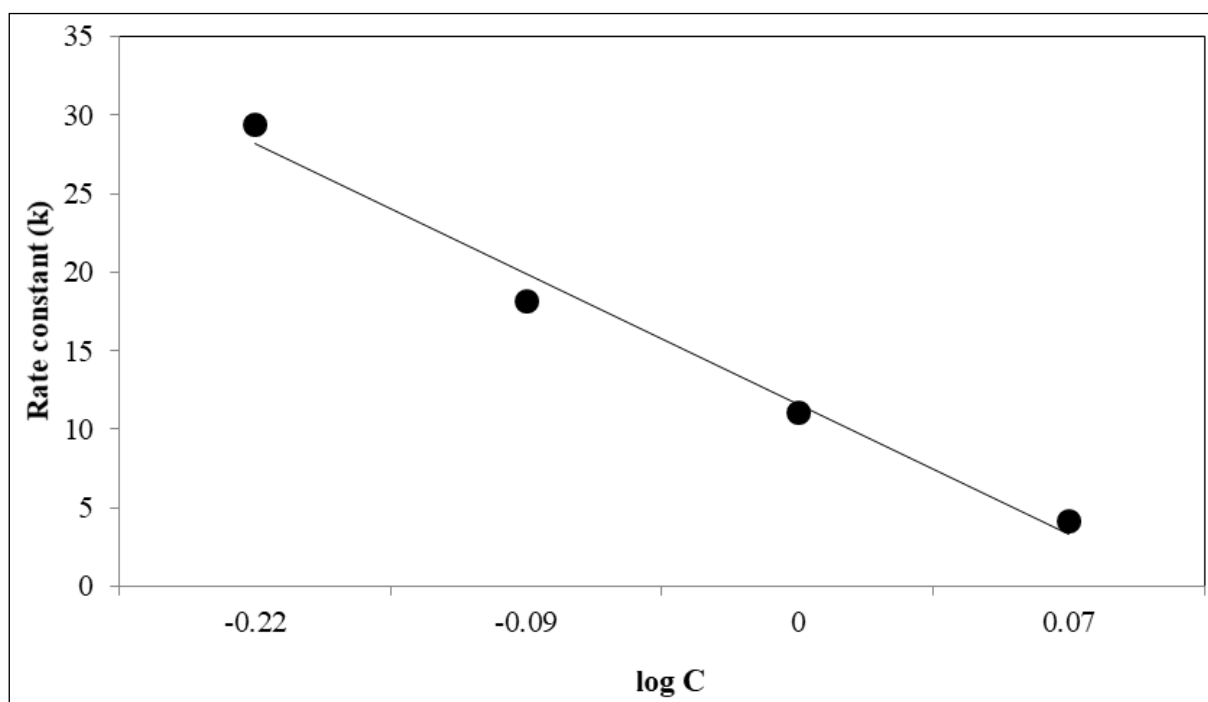
$$t_{1/2} = 0.693 / k \quad (10)$$

where, 't' is time in hours and 'k' is rate constant.

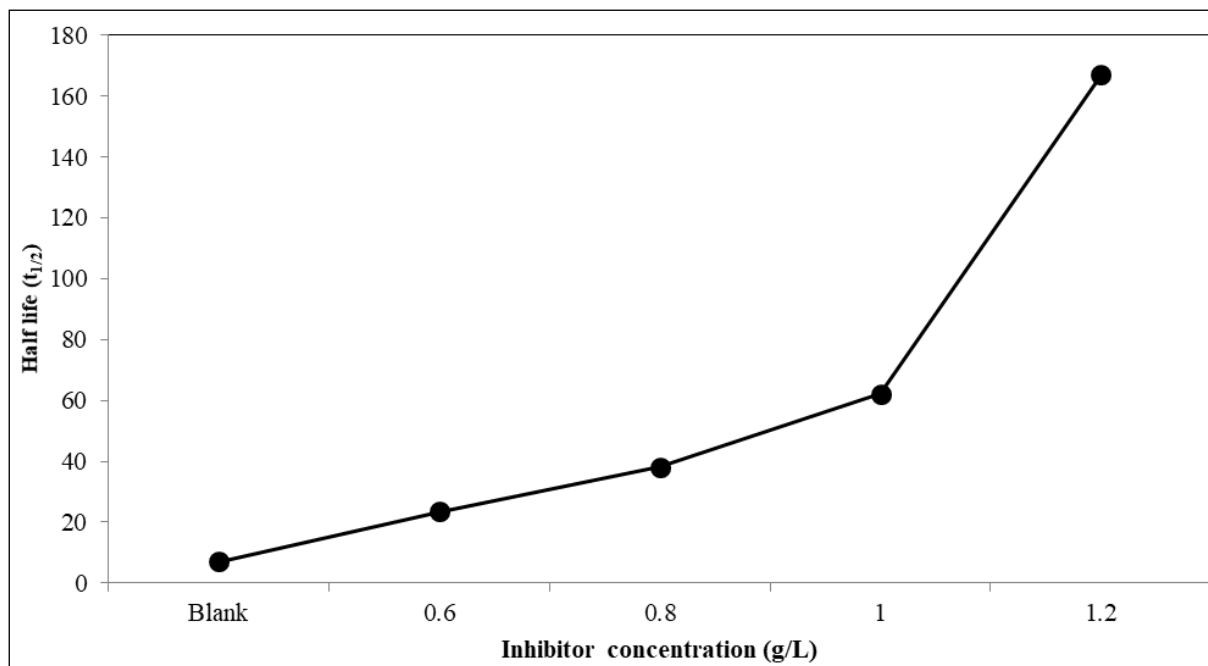
As concentration of inhibitors increases rate constant 'k' decreases (Figure 7) whereas the half-life increases (Figure 8) (Table 4). The results were in good agreement with the result obtained by Muthukumar and Chandrasekaran [27]. Corrosion rate constant 'k' increases with increase in concentration of acid.

**Table 4:** Kinetic data for the corrosion of aluminium in various concentration of HCl containing various concentration of Rose flower extract.

Inhibitor	Inhibitor concentration (g/L)	Acid concentration					
		0.75 M		1.0 M		1.25 M	
		Rate const. ( $k \times 10^{-3}$ ) ( $\text{day}^{-1}$ )	Half life ( $t_{1/2}$ ) (day)	Rate const. ( $k \times 10^{-3}$ ) ( $\text{day}^{-1}$ )	Half life ( $t_{1/2}$ ) (day)	Rate const. ( $k \times 10^{-3}$ ) ( $\text{day}^{-1}$ )	Half life ( $t_{1/2}$ ) (day)
<b>Blank</b>	<b>0.0</b>	99.48	07.00	307.53	22.53	439.41	157.71
<b>Rosa (Rose flower)</b>	<b>0.6</b>	29.45	23.53	94.08	07.36	155.86	04.44
	<b>0.8</b>	18.16	38.16	84.25	08.22	139.27	04.97
	<b>1.0</b>	11.13	62.26	68.72	10.08	120.80	05.73
	<b>1.2</b>	04.15	166.98	53.62	12.92	100.00	06.93



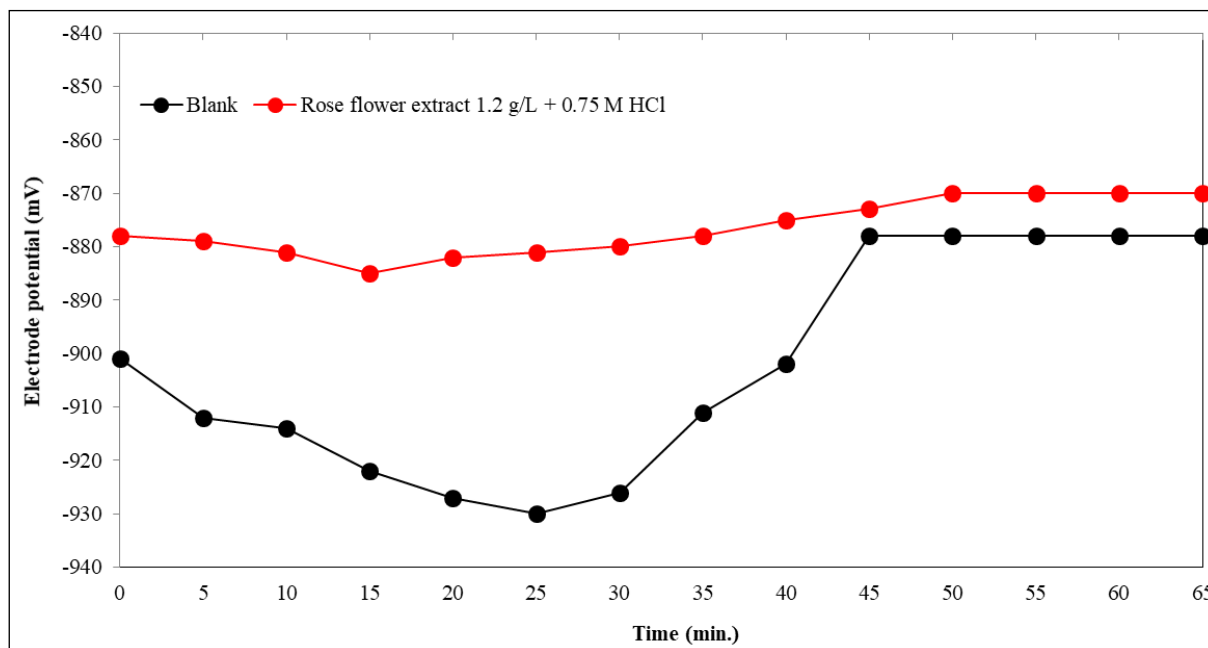
**Fig 7:** Plot of rate constant against log c for aluminium in 0.75 M HCl solution containing Rose flower extract



**Fig 8:** Variation of the Half -life ( $t_{1/2}$ ) with the concentration of extracts of Rose flower for aluminium in 0.75 M HCl solution at room temperature.

#### Open Circuit Potential (OCP) measurement

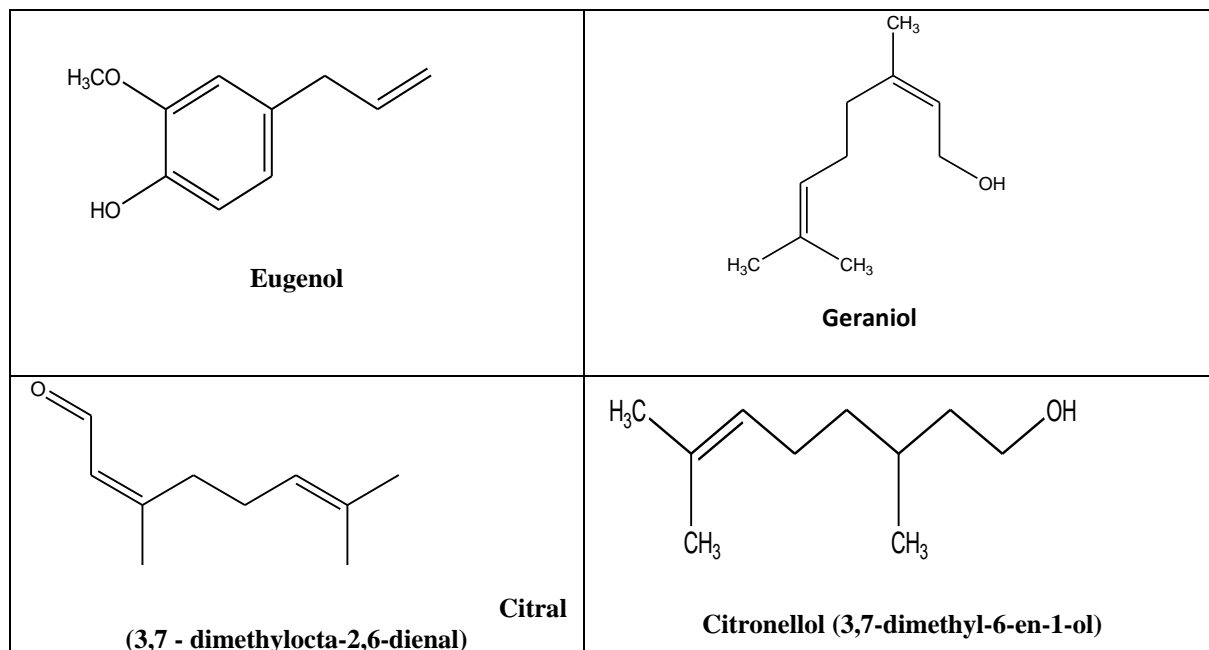
Values of OCP immersed ( $E_{ini.}$ ) and steady state ( $E_{s.s.}$ ) for aluminium in 0.75 M in HCl containing 1.2 g/L rose flower extract at 301 K was shown in Figure 9. It is noted that the initial potential ( $E_{ini.}$ ) value for the corrosive solution without inhibitor gradually decreases (less negative) with time i.e. from -901 mV and stabilizes at -878mV ( $E_{s.s.}$ ) after 45 min. On addition of 1.2 g/L inhibitor the OCP shift from -878 mV ( $E_{ini.}$ ) and attain a steady state -870 mV ( $E_{s.s.}$ ) within 50 min. (both initial and constant OCP) suggesting polarization of local anodes. The shift of OCP in positive direction indicates the interference of these inhibitors with the anodic partial process<sup>[28]</sup> blocking the anodic reaction sites of the metal electrodes<sup>[29]</sup>. It is quite understandable that change in potential with time depends on a number of factors like area of local anodes and cathodes, kinetics of anodic and cathodic reactions, anions present, dissolved oxygen.



**Fig 9:** Electrode potential (mV) of aluminium in 0.75 M HCl containing 1.2 g/L Rose flower extract

#### Mechanism of inhibition by *Rosa* (Rose) flower extract

The I.E. was found up to 95.60 % for 1.2 g/L Rose extract in 0.75 M HCl solution. The main constituents are shown in below Figure 10.



**Fig 10:** Structure of main constituents of Rose flower extract.

Rose contain amino acids, fatty acids, flavonoids, steroids, and other organic substances <sup>[11]</sup>. The main components of Rose flower extract are Eugenol, Geraniol, Citral (3, 7 - dimethylocta-2, 6-dienal), Citronellol (3,7-dimethyl-6-en-1-ol) <sup>[10]</sup>.

The lone pair electrons of O, N, and S atoms can form coordinate covalent bonds to the metal surface. The substances can also be adsorbed on the metal surface due to electrostatic action or the formation of chelates with  $Al^{3+}$ . In addition, extracts containing double bonds can be attracted to the metal surface. The inhibition is due to the adsorption of the inhibitor molecules on aluminium surface and blocking is active sites <sup>[11]</sup>.

### Conclusion

The present study shows that Rose extract was found to be a good eco-friendly inhibitor for the corrosion control of aluminium in HCl solution. As the concentration of Rose flower extract increase corrosion rate decreases while I.E. increases. Rose flower extract shows maximum I.E. of 95.60 % at 1.2 g/L concentration in 0.75 M HCl solution. In Rose flower extract active molecule adsorbed on metal surface follows Langmuir adsorption isotherm. The inhibitory action of Rose flower extract decreased when the temperature increases. Inhibition efficiency increases with an increase in Rose flower extract concentrations in 0.75 M HCl but decreased with rise in temperature. The negative free energy of adsorption  $\Delta G^{\circ}_{ads}$  indicates strong and spontaneous adsorption of the Rose flower extract on the aluminium surface.

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