Study of Anticorrosive behavior of 'Clove oil' on Copper in Acidic Medium

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Abstract- **Corrosion protection properties of clove oil were studied on copper in acidic medium by using weight loss method. Results clearly indicate that efficiency of inhibition increases with increase in clove oil amounts. Inferences show that the clove oil is a perfect inhibitor to prevent copper from corrosion. Equilibrium Constant for adsorption of clove oil on copper was also calculated. Thermodynamic and kinetic parameters were calculated from the experimental readings. These studies reveal that clove oil is a strong clove oil of corrosion of copper by greatly lowering the dissolution currents..**

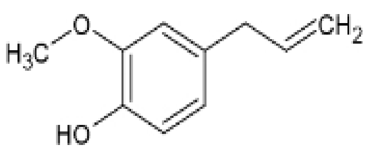
Keywords- Corrosion prevention, Langmuir isotherm, Adsorption, First order Kinetics.

1. INTRODUCTION

Capacity of organic compounds to protect metal from corrosion depends on its adsorption on metal surface [1-2]. Organic compounds having active functional groups with electronegative atoms are contained by clove oil in good amount. [3]. Any organic compound containing hetero-atoms like O, N, S & P in its aromatic rings are the major locations of adsorption which prevents corrosion [4].

2. MATERIALS & METHOD

Clove oil:
Oxygen is the active center in the molecule of clove oil. Clove oil is non hazardous and environment friendly. It is easy to produce and purify clove oil. This created our interest to select Clove oil and study its properties of corrosion prevention of copper in acidic media.



Eugenol

Flower buds of the tree Eugenia caryophyllata are dried and these are cloves. Cloves are ground and subjected to steam distillation to recover clove oil. Clove oil is a mixture of many compounds Eugenol is the main component of clove oil

Molar mass: 164.2g / mol
Density: 1.06 g / cm^3
IUPAC ID: 4 – Allyl-2methoxyphenol
Copper:
Copper occurs in nature in a directly unstable metallic form.
Melting Point: 1357.77 K
Density: 8.96 g / cm^3 at RT
Method: Weight Loss Method [5] with different amount of clove oil and different immersion periods was adopted.

3. EXPERIMENT

Rectangular shaped Copper specimenssized 3×2×0.2 cm were used. The specimens were mechanically rubbed with fine emery paper and were washed with acetone for degreasing
. Finally Specimens were then washed with water and dried at 100°C in hot air oven and cooled to RT by keeping them in desiccators. The clean and dry specimen was now weighed by using digital balance. Heating, cooling and weighing was repeated till constant reading was achieved. Finally Copper specimens were kept in desiccators.
The acid solution was made by distilled water. One specimen was immersed in acid solution without inhibitor. Other specimens were immersed in acid solution with addition of different concentrations of clove oil inhibitor (1g – 4 g / litre) for different period of time (1-4 Days) The specimens were immersed in different solutions with or without inhibitor in with a wire hook in the 100 ml beakers containing 50 ml 0.5N HCl solution and different concentrations (1g-4g/lit) of clove oil at RT. The specimens were taken out of test solutions after completing particular immersion period. These are now washed with distilled water, dried weighed to evaluate weight loss.

4. CALCULATION

Percentage inhibition efficiency for different sets of tests/ studies was calculated with following formula.

$$\% \text{ I E} = [1 - W_1/W_2] \times 100$$

W_1 = weight losses (g) for copper in presence of clove oil in HCl solution.
W_2 = weight losses (g) for copper in absence of clove oil in HCl solution.
The Rate of corrosion (mili miles per year) was calculated with the help of following equation [6].

Corrosion rate = 87.6W / dAt (mmpy / yr)
W = weight loss (g), D = density of the specimen (gcm^{-3}), A = Area of specimen (square cm)
t = exposure time (h).
Coverage area of Surface (θ) was calculated by equation as under.

$$\theta = 1 - W_1/W_2$$

5. RESULTS AND DISCUSSION

Tables (1-4) express all the calculated data of efficiency of inhibition (IE %), Coverage area of Surface (θ) and Rate of corrosion (mmpy) in presence of different amounts of the clove oil in 0.5N HCl for different emersion days (1 to 4). Weight loss data was used to determine all the fields.With the experimental data and calculations it is clear that clove oil has remarkably reduced the Rate of corrosion. The graph (Fig.1) was plotted between concentrations & % I E clearly indicate that corrosion decreases with increasing concentrations of clove oils.The corrosion data matches first order reaction.

Table 1:Efficiency of Inhibition (% I E), Rate of corrosion and Coverage area of Surface (θ) (at RT) (Immersion period: 24 Hours)

Conc. of clove oil (g / litre)	Δ W (g)	% I E	Rate of corrosion (mmpy)	Coverage area of Surface (θ)
-	0.0152	-	7.72	-
1	0.0036	76.31	11.30	0.7631
2	0.0030	80.26	9.41	0.802
3	0.0024	84.21	7.53	0.842
4	0.0019	87.5	5.96	0.875
5	0.0014	90.7	4.39	0.907
6	0.0010	93.42	3.13	0.934

Table 2: Efficiency of Inhibition (% I E), Rate of corrosion and Coverage area of Surface (θ) (at RT) , (Immersion period: 48 Hours)

Conc. of clove oil (g / litre)	Δ W (g)	% I E	Rate of corrosion (mmpy)	Coverage area of Surface (θ)
-	0.0173	-	48.71	-
1	0.0065	62.42	18.30	0.624
2	0.0045	73.98	12.67	0.739
3	0.0038	78.03	10.69	0.789
4	0.0033	80.92	9.29	0.809
5	0.0028	83.81	7.88	0.838
6	0.0021	87.86	5.91	0.878

$$\log (W_i - \Delta W_t) = (-k/2.303)\, t + \log W_i$$

k = Rate constant, W_i= initial weight of copper sample, Δ W_t= weight loss of copper specimen at time t , (W_i - ΔW_t) = Residual weight of copper specimen at time t and is written as W_f (Figs. 2). Rate constants calculated from the slope are written in Table 6. Half life ($t_{1/2}$) was calculated with the formula as under [6].

$$t_{½} = 0.693 / k$$

Rate constant k lowers with raise in amount of clove oil. Half life increases with increase in amount clove oil. Increasing half life verifies corrosion prevention of metal.

Table 3:Efficiency of Inhibition (% I E), Rate of corrosion and Coverage area of Surface (θ) (at RT) (Immersion period: 72 Hours).

Conc. Of clove oil (g / litre)	Δ W (g)	% I E	Rate of corrosion (mmpy)	Coverage area of Surface (θ)
-	0.0211	-	89.11	-
1	0.0071	66.35	29.98	0.663
2	0.0069	67.29	29.14	0.672
3	0.0064	69.66	27.03	0.696
4	0.0055	73.93	23.22	0.739
5	0.0044	79.14	18.58	0.791
6	0.0030	85.78	12.67	0.857

Table 4: Efficiency of Inhibition (% I E), Rate of corrosion and Coverage area of Surface (θ) (at RT) (Immersion period: 96 Hours)

Conc. of clove oil (g / litre)	Δ W (g)	% I E	Rate of corrosion (mmpy)	Coverage area of Surface (θ)
-	0.0316	-	177.95	-
1	0.0126	60.12	70.95	0.601
2	0.0119	62.34	67.01	0.623
3	0.0112	64.55	63.07	0.645
4	0.0099	68.67	55.75	0.686
5	0.0092	70.88	51.80	0.708
6	0.0085	73.10	47.86	0.731

Coverage area of Surface (θ) for different amounts of inhibitor was calculated and verified graphically. The graph between C / θ and C gives straight line (Fig.2). It indicates the coverage of inhibitor on anodic and cathodic areas. This is unilayer adsorption of inhibitor following Langmuir isotherm [6].

$$C / \theta = C + 1 / K_{ad}$$

Kad = Equilibrium constant of adsorption
The corrosion prevention process by adsorption of inhibitor on copper in acidic medium follows Langmuir adsorption isotherm with slope of almost unity. it is clear that single layer of the clove oil is attached to copper surface without lateral interactions between the adsorbed material. Free energy of adsorption ΔG_{ads} was also calculated with the equation as under.

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

R = gas constant, T = temperature, K = equilibrium constant of adsorption
ΔG_{ads} values shown in Table 6 are Negative values which reflect continuous adsorption and stable layer of adsorbed inhibitor on the copper.

Table 5:Kinetic parameters

Concentration of clove oil (g / litre)	k (s^{-1})	$t_{½}$ (s)
0	12.7×10-7	5.56×105
1	6.7×10-8	1.03×107
2	4.5×10-8	1.54×107
3	4.4×10-8	1.57×107
4	3.3×10-8	2.10×107
5	2.1×10-8	3.3×107
6	1.9×10-8	3.6×107

Table 6:Langmuir adsorption parameters for different immersion periods.

Time (no. of days)	K_{ad}	Slope	$-\Delta G_{ads}$	R^2
1	2.74	1.038	25.11	0.996
2	1.52	1.045	18.06	0.988
3	1.21	1.050	15.91	0.982
4	2.79	1.250	24.11	0.986

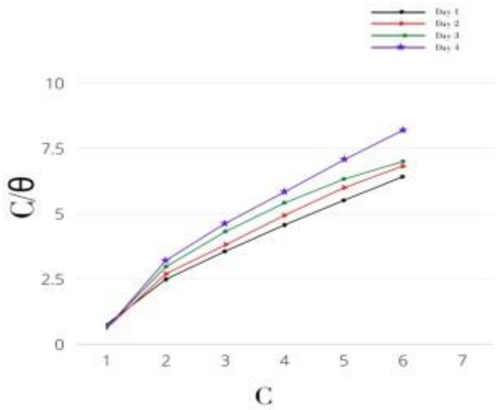


Fig 1: Variation in efficiency of inhibition with different amounts of clove oil (immersion period: 1- 4 days)

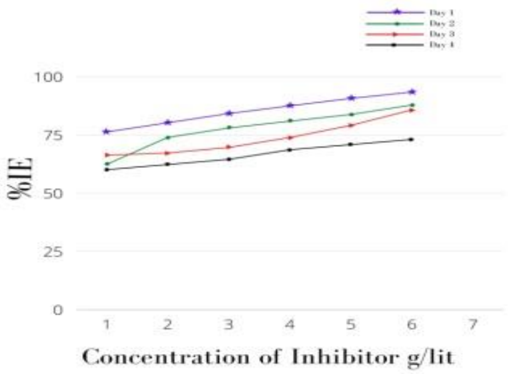


Fig 2: Langmuir adsorption isotherm for different immersion Periods

6. CONCLUSION

Clove oil is a very good inhibitor of corrosion of copper. It inhibits corrosion up to 98% at RT. Kinetics of Clove oil on copper follows first order reaction. The isotherm is of Langmuir adsorption isotherm. The negative values of ΔG_{ads} revels continuous adsorption and stable layer of corrosion product is formed on copper. Clove oil herbal, natural, green and environmental friendly which does not have any health hazard therefore it is a very good and potential inhibitor of copper.

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