Research Article

Inhibition of Zinc by Natural Oil in 0.5N Hydrochloric Acid and 0.5N Sulfuric Acid

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ABSTRACT

Consequence of *Helianthus annuus* oil on corrosion of zinc metal in Hydrochloric acid and Sulfuric acid by weight loss method was investigated with and without of oil. It has been found that inhibition efficiency increases with amount of *Helianthus annuus* oil in 0.5N Hydrochloric acid and 0.5N Sulfuric Acid. *Helianthus annuus* oil was found more effective in 0.5N Hydrochloric acid than 0.5N Sulfuric acid. Different adsorption isotherm shows that *Helianthus annuus* oil physical adsorbed on metal. Kinetics and thermodynamics parameters also have been concluding in 0.5N Hydrochloric acid and 0.5N Sulfuric acid.

Keywords: Weight loss, *Helianthus annuus,* Adsorption Isotherms, Kinetics.

INTRODUCTION

Acid solutions are often used in industry for pickling, decaling and cleaning of metals structures, processes which are normally accompanied by considerable dissolution of the metal. A useful method to protect metals deployed in service in such aggressive environments against corrosion is the addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. A number of organic compounds are known to be applicable as corrosion inhibitors for metal in acidic environments.[1-8] Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrosion attack. However, there is increasing concern about the toxicity of most corrosion inhibitors. The toxic effect does not only affect living organisms but also poison the environment. Due to the toxicity of some corrosion inhibitors, there has been increasing search for green corrosion inhibitors. Inhibitors in this class are those that are environmentally friendly and are gotten from natural products such as plant extracts and natural seeds oil. Several studies have been carried out on the inhibition of corrosion of metals by plant extract and natural seeds oil. [9-12] *Helianthus annuus* oil is one of the non-volatile oil, expressed from *Helianthus annuus* seeds. The oil of *Helianthus annuus* is rich in Palmitic acid 4 - 9%, Stearic acid 1 - 7%, Oleic acid 14 - 40%, Linoleic acid 48 -74% according to British Pharmacopoeia. *Helianthus annuus* oil contains predominantly linoleic acid in triglyceride form. The object of the present work to study the effects of *Helianthus annuus* oil on corrosion in 0.5N HCl and 0.5N H_2SO_4 solution by using gravimetric method. Thermodynamic and kinetic parameters were estimate and discussed in absence and presence of *Helianthus annuus* oil.

MATERIALS AND METHODS

Material preparation

The sheet of zinc of thickness 0.2 cm and chemical composition of Zinc specimens – 1.03% Pb, 0.04% Cd, 0.01% Fe and balance part zinc have been used for the experimental method. The zinc was mechanically press-cut into 3 X 2 cm coupons; they were degreased in acetone, rinsed with double-distilled water, dried in oven and then stored in calcium chloride moisture free desiccators. The *Helianthus annuus* used as inhibitor was obtained from sunflower plant seeds.

Weight loss determination

The weight loss was determined following the method reported earlier.[13] Sets of experiments were carried out consisting of 50ml beakers, previously weighed zinc coupons were each suspended in each beaker with the help of glass hooks. The zinc coupons were retrieved from the acidic solutions at 1hours. Each retrieved coupon was scrubbed several times to remove corrosion product, dried in oven, reweighed and weight loss was calculated in grams. Experiments were repeated with the inhibitor different concentrations.

The weight loss which was used to compute the corrosion rate given by:

$$\text{Corrosion Rate (mmpy)} = \frac{87.6\,W}{dAt} \qquad (1)$$

Where W is the weight loss (milligrams), d is the density of the specimen (g/cm^3), A the area of the specimen (square inch) and *t* the exposure time (hrs).

The inhibition efficiency of sunflower oil acting as inhibitor in 0.5 N HCl and 0.5N H_2SO_4 were calculated using the following expression:

$$\%IE = 1 - \frac{W_i}{W_0} \times 100 \quad (2)$$

Where W_o and W_i are the weight losses of the zinc coupons in the absence and presence of inhibitors, respectively, in 0.5N HCl and 0.5N H_2SO_4 at the room temperature. The degree of surface coverage (θ) was calculated from equation (3)

$$\theta = 1 - \frac{W_i}{W_o} \quad (3)$$

RESULTS AND DISCUSSION

Corrosion rates and inhibition efficiency

Inspection of Table 1 shows the corrosion rate against inhibitor concentration for zinc corrosion in 0.5 N HCl and H_2SO_4 from weight loss measurements. The Table reveals that the rate of corrosion of zinc in 0.5 N HCl and 0.5N H_2SO_4 decreases with increase in inhibitor at all inhibitor concentrations studied. The increase in inhibition efficiency with increase in concentration of the oil can be explained on the basis of increased adsorption of the compound on the metal surface. As observed from Table 1, the corrosion attack of the uninhibited acid on zinc surface was in the order HCl > H_2SO_4, because of the more corrosion nature of chloride ion. The data of Table 1 reveled that *Helianthus annuus* oil behaves in 0.5 N HCl better than 0.5N H_2SO_4, because chloride ions being less hydrated than sulphate ion are strongly adsorbed on the metal surface by creating an excess negative charge towards the solution phase. The process of adsorption of inhibitors are influenced by the nature of the metal surface, the chemical structure of the inhibitor, the type of the aggressive electrolyte and the interaction between inhibitor molecules and the metallic surface. The possibility of cation adsorption by means of electrostatic forces is determined by the electric charge of the metal surface with respect to the solution. Since zinc surface contained positive charges acid media, the good inhibitive properties of the *Helianthus annuus* oil in HCl could be explained by the occurrence of joint adsorption between the cationic species and Cl^- ions. On the other hand, the situation in H_2SO_4 inhibited solutions is different as the heavily, large hydrated ions of sulphate are weakly adsorbed on the zinc surface. [14]

Table 1: %IE, corrosion rate and surface coverage (at room temperature) obtained from weight loss method for zinc in 0.5N HCl (Immersion time: 1h)

Conc. of inhibitor (g/lit)	ΔW(g) with 0.5N HCl	ΔW(g) 0.5N H_2SO_4	%IE with 0.5N HCl	%IE with 0.5N H_2SO_4	Corrosion rate (mmpy) with 0.5N HCl	Corrosion rate (mmpy) with 0.5N H_2SO_4	Surface coverage (θ) with 0.5N HCl	Surface coverage (θ) with 0.5N H_2SO_4
-	0.0189	0.0169	-	-	124.78	111.58	-	-
1	0.0065	0.0075	65.60	55.62	42.91	49.51	0.6560	0.5262
2	0.0045	0.0058	76.19	65.68	29.71	38.29	0.7619	0.6568
3	0.0033	0.0045	82.53	73.37	21.78	29.71	0.8253	0.7337
4	0.0025	0.0039	86.77	76.92	16.50	25.74	0.8677	0.7692
5	0.0020	0.0033	89.41	80.42	13.20	21.78	0.8941	0.8047
6	0.0017	0.0028	91.00	83.43	11.22	18.48	0.9100	0.8343

Kinetics of the corrosion inhibition of zinc in HCl and H_2SO_4 by *Helianthus annuus* oil

The corrosion of zinc in 0.5N HCl and 0.5N H_2SO_4 solution is a heterogeneous, composed of anodic and cathodic reactions. Based on this, kinetic analysis of the data is considered necessary and kinetics of corrosion reaction can be represented by following equation

$$\log \frac{Wi}{\Delta Wt} = -\frac{k}{2.303}\, t + \log Wi \quad (4)$$

Where k is the first order rate constant, W_i is the initial weight of zinc sample Δ W_t is the weight loss of zinc sample at time t and the term (W_i - ΔW_t) is the residual weight of zinc sample at time t and can designated as W_t.

In the present study, the original weight of zinc coupon at time, t is designated W_i, the weight loss is ΔW_t and the weight change at time t, (W_i - ΔW_t). The plots of a linear log (W_i - ΔW_f) against time (seconds) at room temperatures studied, showed variation which confirmed a first order reaction kinetics with respect to the corrosion of zinc in HCl and H_2SO_4 solutions at room temperature without inhibitor (figure 1 and 2). There is a general decrease in the rate constants with increasing concentrations of the additives Tables 2. The increase in half-life ($t_{1/2}$) shown when the additives are present further supports the inhibition of zinc in 0.5 N HCl and 0.5N H_2SO_4 Tables 2. The increase in half life indicates more protection of the metals by the additives .[15]

Table 2: Kinetic parameters for the corrosion of zinc in varying concentration of *Helianthus annuus* oil with 0.5N HCl.

Concentration of inhibitor(g/lit)	K (s^{-1}) with 0.5N HCl.	t ½ (s) with 0.5N HCl.	K (s^{-1}) with 0.5N H_2SO_4	t ½(s) with 0.5N H_2SO_4
0	11.51×10^{-8}	6.02×10^{6}	11.51×10^{-8}	6.02×10^{6}
1	4.606×10^{-8}	1.50×10^{7}	4.606×10^{-8}	1.50×10^{7}
2	4.606×10^{-8}	1.50×10^{7}	4.606×10^{-8}	1.50×10^{7}
3	4.606×10^{-8}	1.50×10^{7}	4.606×10^{-8}	1.50×10^{7}
4	2.303×10^{-8}	3×10^{7}	2.303×10^{-8}	3.0×10^{7}
5	2.303×10^{-8}	3×10^{7}	2.303×10^{-8}	3.0×10^{7}
6	9.212×10^{-9}	7.5×10^{7}	2.303×10^{-8}	3.0×10^{7}

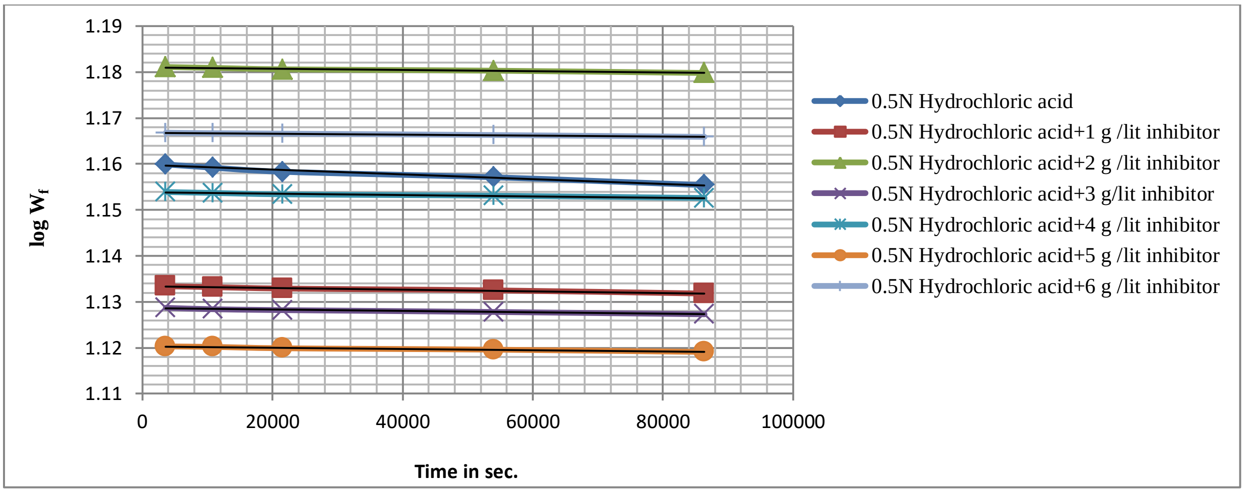

Figure 1: Kinetics plot for the corrosion of zinc in 0.5N HCl with and without inhibitor

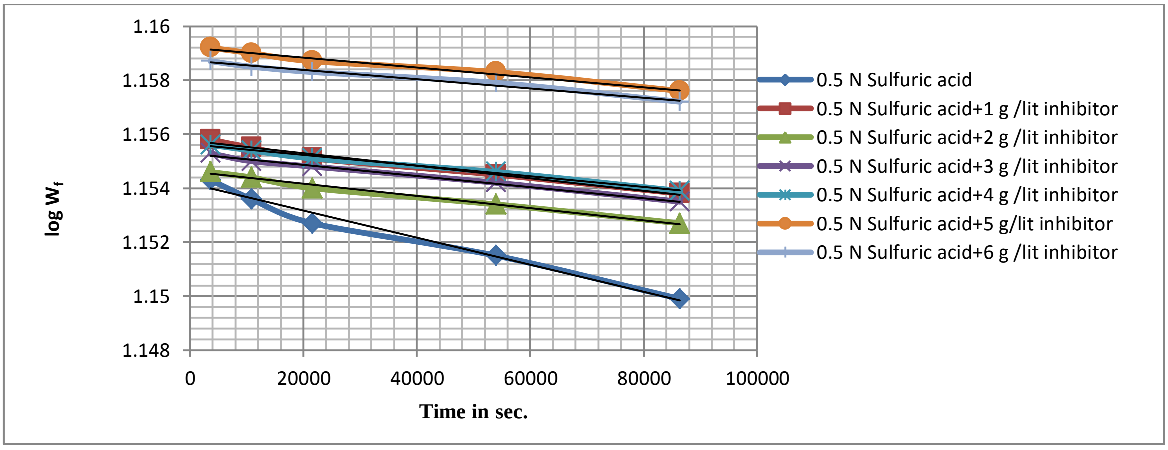

Figure 2: Kinetics plot for the corrosion of zinc in 0.5N H_2SO_4 with and without inhibitor

Thermodynamic and adsorption consideration

The results revealed that the adsorption characteristics of *Helianthus annuus* oil on zinc surface are best described by Langmuir adsorption isotherms. It was shown that the inhibitor acts via a simple adsorption mode. Thus, the apparent corrosion rate of the inhibited zinc electrode is proportional to the ratio of the surface covered θ and that not covered (1 – θ) by the inhibitor. Surface coverage θ values have been evaluated for different concentrations of the *Helianthus annuus* oil under study from corrosion rates in uninhibited and inhibited solutions by means of the equation (3).

The Langmuir adsorption isotherm may be expressed as:

$$C/\theta = 1/k + C \quad (5)$$

Where *K* is the equilibrium constant for the adsorption process, c is the concentration of the inhibitor and θ is the surface coverage.

It was found that Figure 3 and 4 (plot of c/ θ versus *c*) gives straight lines with slope, practically equal to unity, indicating that the adsorption of compound under consideration obeys Langmuir's adsorption isotherm. The deviation of the slope from unity is attributed to the difference in the rate of interaction between the adsorbed species on the metal surface. The interaction between the adsorbed species is not taken into account during derivation of the Langmuir isotherm equation, while the interaction between adsorbed *Helianthus annuus* oil, with polar atoms or groups on the anodic and cathodic sites of the metal surface plays a crucial role. This interaction may be either mutual repulsion or attraction. From the intercept of the straight line on the c / θ axis, it is possible to deduce the value of *K.*

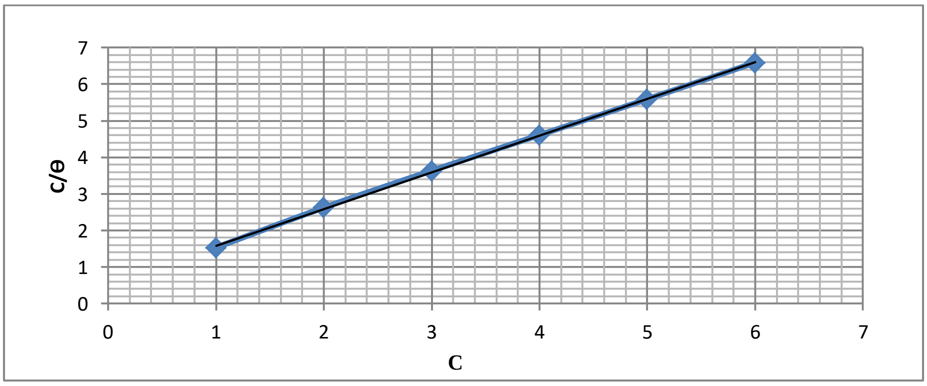

Figure 3: Langmuir adsorption isotherm for zinc in 0.5N HCl with *Helianthus annuus* oil (immersion time 1h)

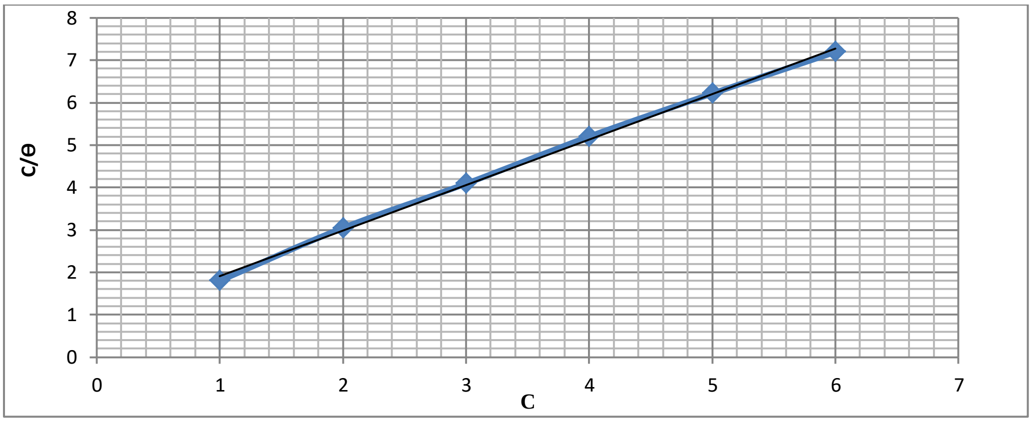

Figure 4: Langmuir adsorption isotherm for zinc in 0.5N H_2SO_4 with *Helianthus annuus* oil (immersion time 1h)

Table 3: Langmuir adsorption parameters for the adsorption of *Helianthus annuus* oil on the surface of zinc in 0.5N HCl and 0.5N H_2SO_4

Temperature (k)	K_{ad}		Slope		$-\Delta G_{ads}$		R^2	
	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4	HCl	H_2SO_4
298	1.7211	1.20	1.004	1.073	19.748	16.77	0.999	0.998

The average values for free energy of adsorption (ΔG_{ads}), calculated using the following equations 5 are given in Tables 3.

$$\Delta G_{ads} = -RT \ln (55.5K) \quad (5)$$

K is the equilibrium constant, R is a gas constant and T is the temperature. It is found that the ΔG_{ads} values for the studied compound are less than -40 kJ mol^{-1}, indicating that the sunflower oil are physically adsorbed on the metal surface.

The low and negative value of ΔG_{ads} indicates the spontaneous adsorption of the inhibitor on the surface of zinc .[16-18]

CONCLUSIONS

Based on the above results, the following conclusion can be drawn:

1. *Helianthus annuus oil* was found to be an excellent inhibitor for zinc in 0.5N HCl better than 0.5NH_2SO_4.
2. Inhibition efficiency increased with an increase in *Helianthus annuus* content up to 6g/l to reach 91% in 0.5N HCl and 83.43% in 0.5N H_2SO_4 at room temperature.
3. Kinetics analyses of data showed linear variations, which confirm a first order kinetic in both the acidic medium.
4. The corrosion process is inhibited by adsorption of the *Helianthus annuus* on the zinc surface following the Langmuir adsorption isotherm.
5. The values of free energy (ΔG_{ads}) of adsorption indicate physically adsorbed and spontaneous adsorption of the *Helianthus annuus* on the zinc surface.

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