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Testing Of Eco-Friendly Compound As Acid Corrosion Inhibitor For Mild Steel



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ABSTRACT

Attempts are made to utilize the aqueous extract of natural compound, namely Date Pits (DP, hard stone of date palm) as acid corrosion inhibitor for mild steel. The inhibition efficiency is evaluated by different techniques; as weight loss, polarization measurements (Tafel plot and Linear polarization) and scanning electron microscope (SEM).

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INTRODUCTION

Corrosion of steel in acid solution has practical importance such as the acid pickling, chemical cleaning of scale in metallurgy, acidizing in oil recovery and other petrochemical processes^[1]. Chemical compounds which will act as corrosion inhibitors are added to the operating medium for controlling the undesired dissolution of the base metal. These inhibitors may be organic or inorganic compounds. They help to reduce metal dissolution to control both hydrogen diffusion and corrosive attack on the metal surface^[2]. The reduction of corrosion rate may be

due to direct action of the compounds added to the aggressive acid solution forming an oxide film or coating on the base metal surface^[3]. On the other hand the inhibiting action may be a consequence of reduction, hydration and/or polymerization reactions of the initial compound^[4].

The use of some chemical compounds as corrosion inhibitors which had toxic effects on the environment was restricted^[5]. The recent trend in the subject of corrosion inhibitors that certain natural products like peels, seeds, fruit-shells and leaves, that contain different organics compounds, (e.g. amino acids, alkaloids, flavonoids, pigments, tannins etc.)

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Which suppress the dissolution reaction of metals^[6] and prevent the environmental pollution^[7]. Many researches^[8,9], has confirmed the use of aqueous extracts of some materials widely available at low cost, as corrosion inhibitors for metal dissolution and cooling systems employing mild steel. These compounds were found to be non-toxic to the environment.

In the present work, the action and effectiveness of aqueous extract of Date Pits (DP) on inhibiting the corrosion of mild steel in acidic media has been studied. Inhibition was studied in hydrochloric and sulfuric acid solutions by gravimetric and electrochemical polarization methods with the aid of a scanning electron microscope (SEM).

EXPERIMENTAL

Inhibitor preparation

The inhibitor solution of Date Pits (which is the waste product of the date palm) were prepared by extracting 10 grams of the dried and crushed Date Pits with about 250 ml boiling distilled water. The procedure was repeated 5 times and the collected extract was filtered and concentrated to 100ml. The extract was kept in the ice chest. It can also be preserved at room temperature in the presence of 0.1% sodium benzoate. Over a period of 6 months, the inhibitive efficiency of the extract was not significantly affected. The chemical analysis of aqueous extract of Date Pits shown that it contains Tannins, Saponas, Glycosides, Steroid and Amino acids compounds and it's pH equal 5.5.

Test specimens preparation

Samples of mild steel have the following composition: C=0.1%, Mn=0.25%, Si=0.01%, P=0.01%, S=0.018%, Cu=0.15%, Cr=0.02%, Ni=0.2% and the remainder is iron. Mild steel specimens (5 x 2.5 x 0.2 cm) were polished using different grades of emery papers, degreased by acetone and finally rinsed by distilled water. All chemicals used in this investigation were from analytical grade.

Weight loss measurements

Inhibition efficiencies for different concentration

of the inhibitor were calculated by weight loss values, in the absence and presence of the inhibitor in 5% HCl and 5% H₂SO₄ at temperature 30°C for 1h.

Inhibition efficiencies of the optimum dose of inhibitor were calculated from weight loss measurements in 5 % HCl and 5 % H₂SO₄ at different temperatures (30, 45 and 60°C) and different time from ½ - 2 h. All experiments weight loss measurements were done in a controlled thermostatic water bath with ±1°C accuracy. The inhibition efficiency (IE %) was calculated from weight loss using the following equation:

$$IE \% = [(W_{\text{free}} - W_{\text{inh}}) / W_{\text{free}}] \times 100$$

Where; W_{free} : weight loss of test specimen in test solution in the absence of inhibitor.

W_{inh} : weight loss of test specimen in test solution in the presence of inhibitor.

Electrochemical measurements

Studies were carried out in a conventional glass cell with a platinum counter electrode and a saturated calomel reference the Polarization electrode (SCE). The working electrode was a sheet cut from mild steel with 2 cm² exposed surface area. The polarization measurements were carried out in test solution of 5% HCl and 5% H₂SO₄ in absence and in the presence of the inhibitor. The Polarization resistance and Tafel line values were measured by using potentiostat model 273/81 at 1.66 x 10⁻⁴ mV/s scan rate under static conditions.

RESULTS AND DISCUSSION

Weight loss measurements

Figure 1 shows the effect of inhibitor concentration on the inhibition efficiency (IE%) using weight loss measurements in 5 % HCl and 5 % H₂SO₄ at 30°C for immersion time 1h. The inhibition efficiency increases with increasing the concentration of DP and it reaches the maximum values 87% in 5 % HCl and 72% in 5 % H₂SO₄. The maximum inhibition efficiency of DP was achieved at 4 ml (vol/vol %) in both 5 % HCl and 5% H₂SO₄. Further increase of inhibitor concentration did not cause any appre-

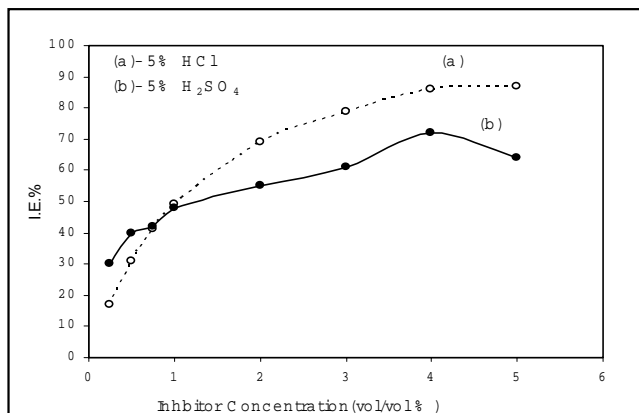


Figure 1: Inhibition efficiency IE of DP inhibitor as function of concentration for mild steel for 1h. at room temperature.

ciable change in the performance of the inhibitor. This result reveal that, the DP extract acts as a good corrosion inhibitor for the acid corrosion of mild steel. Such a good corrosion inhibition can be attributed to the adsorption of the inhibitor on the mild steel surface^[6,10,11,12].

Figure 2 shows the effect of immersion time on the performance of inhibitor at its optimum dose 4 ml (vol/vol%) and temperatures 30 and 45°C in 5 % HCl and 5 % H₂SO₄. The curves (a) and (b) show maximum inhibition efficiency (87% and 72%) after 1h. This good performance is not changed until 2h. It has been observed that the inhibition efficiency of the inhibitor decreases with increasing the temperature from 30 to 45°C. This is due to the desorption of the inhibitor molecules from the mild steel surface^[13]. It was found that at 60°C the inhibition efficiency was deteriorated, this can be correlated to dissolution of the test specimen which increasing the real surface area of the test specimen with time^[14].

Figure 3 shows the effect of acid strength on the inhibition efficiency of the test inhibitor at its optimum dose for 1h at room temperature. It has been observed that the inhibition efficiency was affected adversely by increasing acid strength from 5% to 7% and 10%.

Potentiodynamic polarization studies

Figures 4(A, B) shows the potentiodynamic polarization curves of mild steel in the absence and presence the optimum dose of inhibitor (4ml) at room

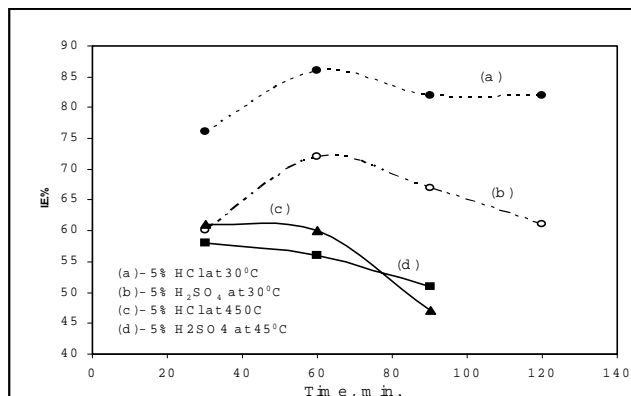


Figure 2: Effect of immersion time on IE of DP inhibitor for mild steel

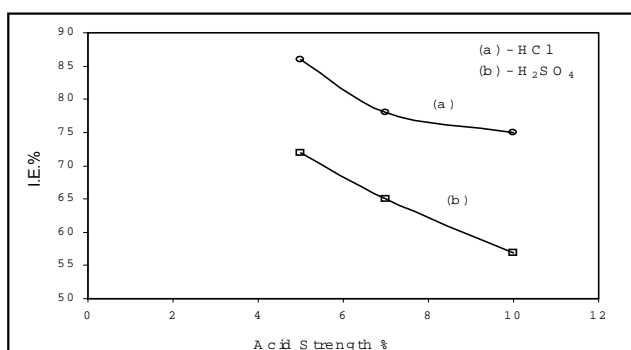


Figure 3: Effect of acid strength on the IE of DP inhibitor for mild steel at room temperature

temperature in 5% H₂SO₄ and 5% HCl, respectively. Figure 4A-curve b (5% H₂SO₄ + inhibitor) shows that the presence of inhibitor shifts the corrosion potential (E_{corr}) towards noble values. The inhibitor has a pronounced effect on the mild steel, particularly at the anodic potential. The inhibition efficiency is higher on the anodic side than the cathodic one, indicating that the anodic partial process is much more affected than the cathodic partial one^[15]. Figure 4B-curve b (5% HCl + inhibitor) shows that the corrosion potential (E_{corr}) shifts to more negative values. The inhibitor acts as predominantly anodic inhibitor in case of 5% H₂SO₄, while acts as a cathodic one in case of 5% HCl.

TABLE 1 illustrates the various electrochemical parameters, the polarization resistance (R_p), corrosion current (I_c), corrosion potential (E_c), corrosion rate (CR) and inhibition efficiencies percent (IE%) which are calculated by Tafel plot (T.L.), Linear polarization (L.P.) and Weight loss (W.L.) methods at room temperature in 5% H₂SO₄ and 5% HCl solu-

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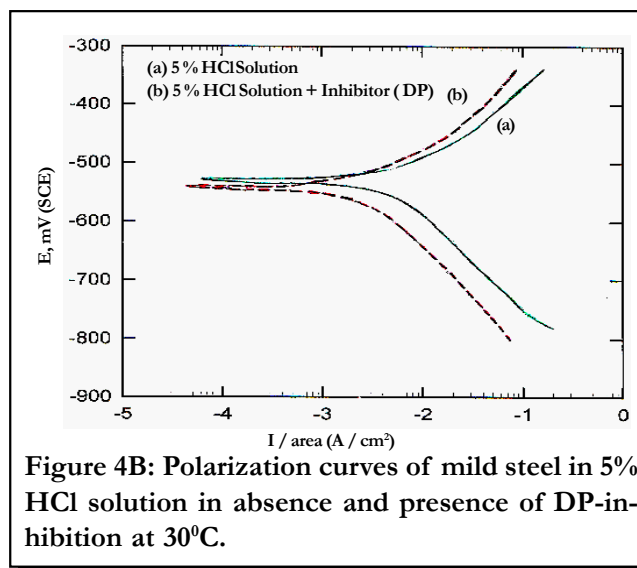
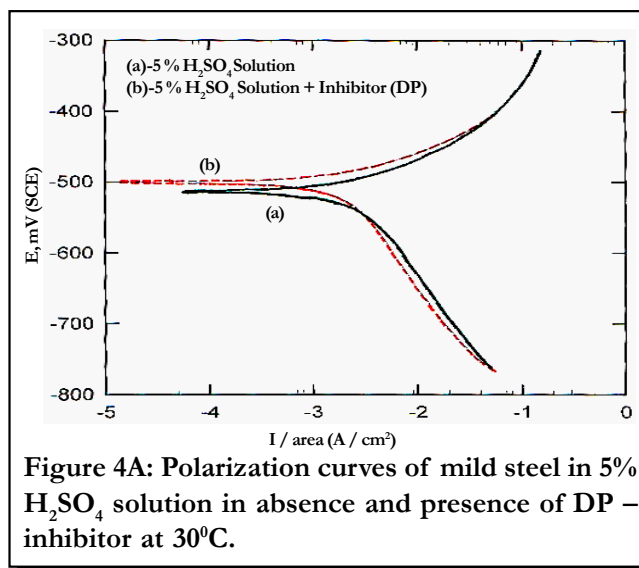


TABLE 1: Electrochemical data and the inhibition efficiencies

Acid	Inh.Dose. vol/vol %	β_a V/decade	β_c V/decade	$E_{\text{corr.}}$ mV/SCE	I_{corr} mA/cm ²	C.R. mpy	R_p Ω	I.E %		
								T.L.	L.P.	W.L.
5% HCl	Blank	$10^3 \times 129.6$	$10^3 \times 191.2$	-527.7	6.37	$10^2 \times 45.6$	5.02			
	4ml	$10^3 \times 135.7$	$10^{-3} \times 202$	-543	1.88	$10^2 \times 6.3$	9.8	70.4	95.2	87
5% H_2SO_4	Blank	$10^3 \times 114.5$	$10^3 \times 273.4$	-513.6	4.25	$10^2 \times 53.5$	7.64			
	4ml	$10^3 \times 97.3$	$10^3 \times 259.4$	-500.8	1.53	$10^2 \times 15.7$	13.35	64	74.7	72

tions.. It is observable that, in the presence of inhibitor, E_c shifts to more positive values in case of 5% H_2SO_4 , while in case of 5% HCl the potential shifts in the cathodic direction. Furthermore, the values of R_p increase, while the values of I_c decrease with inhibited HCl and H_2SO_4 , the inhibitor causes a shift of the polarization curves towards lower current density values (I_{corr}) thus affecting the rate of both the anodic and cathodic processes, hence the I_{corr} decreases significantly. It may be observed that, in nearly all cases, changes in the slope of the Tafel plots caused by the presence of the inhibitor are not significant enough to suggest a change in the mechanism of the anodic and cathodic processes.

The polarization resistance (R_p) value can help us to assess the relative ability of material to resist corrosion. The polarization resistance is inversely proportional to corrosion current so the materials with the highest R_p have the highest corrosion resistance. From these facts, we can discuss and correlate the data obtained from the polarization resistance (R_p) and those computed from Tafel plots.

From the data depicted in TABLE 2, it has been found that, the addition of DP (optimum dose) as inhibitor to acid solutions (5 % H_2SO_4 and 5 % HCl) enhanced the corrosion inhibition efficiency of mild steel compared with the acid free inhibitor. The inhibition efficiencies calculated from Tafel plot, linear polarization and weight loss methods are in good agreement. These types of comparison between the inhibitor efficiencies evaluated by the three methods have also been explained by several other workers in the literatures^[16,17,18].

Aggressive ions (Cl^- , SO_4^{2-}) can be adsorbed on active sites, randomly distributed on the steel surface and then desorbed with the surface cation. The drastic decrease in the R_p and increase in I_c of steel in additive free H_2SO_4 and HCl solutions can be ascribed to the dissolution of steel due to the formation of FeCl_3 and FeSO_4 . In case of addition the inhibitor (especially optimum dose) competitive surface adsorption between the aggressive ions and the inhibitor molecules is assumed to occur^[19,20] but the additive have almost covered the surface of steel,

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hence the process of corrosion is decreased. So, the decrease in corrosion rate is associated with an increase in R_p values and a decrease in I_c values with optimum dose. The results of these studies have shown that, the inhibition of the optimum dose suggests an appreciable contribution to inhibition process via interaction of DP molecules with the electrode surface^[21]. Moreover, this behavior may be ascribed to the facilities of adsorption of the DP molecules, so enhancing the corrosion inhibition efficiency^[22]. Adsorption of this compound may occur through their active centres ^[12].

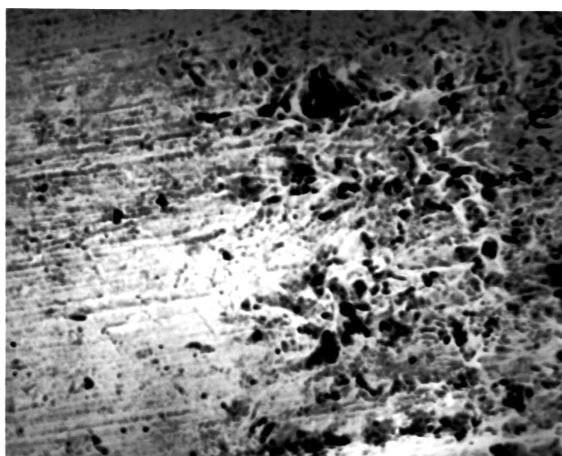
SURFACE MORPHOLOGY EXAMINATION

Morphology of mild steel surfaces treated in 5 % HCl and 5 % H_2SO_4 in the absence and presence

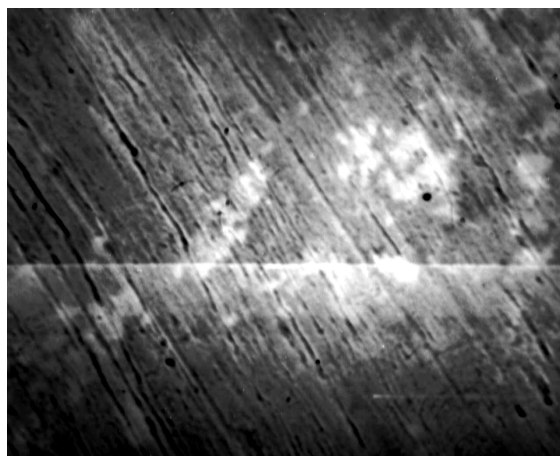
of DP (optimum dose) for 1h, at room temperature were studied using the scanning electron microscope (SEM). The results of these investigation are shown in figure 5 (A – D).

Figures 5A and 5B show that samples treated in 5 % HCl and 5 % H_2SO_4 solutions in the absence of DP respectively, have some of corrosion areas on its polished surface. The presence of such regions can be attributed to the dissolution of mild steel due to the surface attack by the aggressive ions.

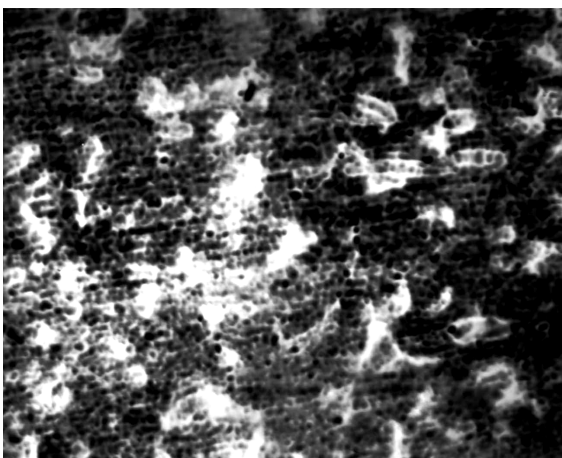
It is obvious from figures 5C and 5D that samples treated in 5 % HCl and 5 % H_2SO_4 solutions in the presence of DP respectively, are improved in the surface morphology. This due to the coverage of the surface by a protecting film and hence a more homogenous surface is formed. This explains why the corrosion rate in the extract inhibitor containing



(A) (X500) corroded sample immersed in 5% HCl in absence of DP.



(C) (X-500) inhibited sample immersed in 5% HCl containing DP.



(B) (X-500) corroded sample immersed in 5% H_2SO_4 Solution .



(D) (X-500) inhibited sample after 1h. immersed in 5% H_2SO_4 containing DP

Figure 5: SEM micrographs of mild steel in 5% HCl and 5% H_2SO_4 solutions for 1h at room temperature

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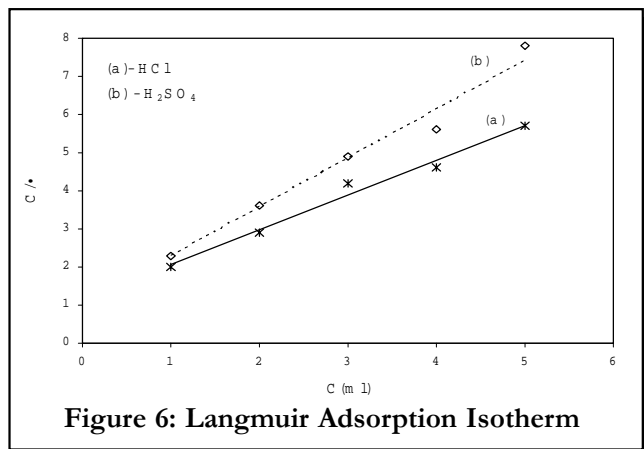


Figure 6: Langmuir Adsorption Isotherm

solutions is lower than that measured in inhibitor free solutions.

In view of many investigations carried out^[3,8,23] concerning the beneficial effect of organic compounds as corrosion inhibitors and the nature of adsorption of organic inhibitor,^[1,24,25] we will try to explain the mechanism of inhibition effect of DP in the present results.

The obtained data shows that, most of organic inhibitors act by adsorption on the steel surface. For the studied inhibitor, it was found that the experimental data fits Langmuir's adsorption isotherm (Figure 6). This phenomenon is influenced by the nature and surface charge of metal, the type of aggressive electrolyte and the chemical nature of the inhibitors. Most organic inhibitors are substances with at least one functional group considered as the reaction center for the adsorption process. The adsorption of inhibitor is related to the presence of heteroatoms as nitrogen, oxygen, phosphorous and sulphur as well as triple bond or aromatic ring in their molecular structure.

Mann^[26] has suggested that organic substances forming onium ions in acidic solutions are adsorbed on the cathodic sites of the metal surface and interfere with the cathodic reaction.

In another view, some authors^[12,27,28] suggested that, amine type inhibitors have electron - donating ability and could be adsorbed on metal (M) by electron - donation of the N-atom (M: NH₂R), and by bridging with the active hydrogen atom attached to the N-atom (M: HNHR).

In agreement with some author^[8,12,23,27,29] the con-

stituents of examined extract are mostly composed of oxygen and nitrogen containing compounds. Most of the oxygen containing constituents of the extracts are hydroxy aromatic compounds, e.g. tannins, pectin, flavonoids, steroids and glycosides. Adsorption of these constituents may occur through their N and O active centres.

Similar conclusions were reached by Sola et al^[30], that numerous OH- groups around the molecules make them more ready to form strong links with hydrogen. In addition they can form complex with or around the metallic cations. These complexes can cause blocking of micro-anodes and/or micro-cathodes that are generated on the metal surfaces when they are in contact with electrolyte, and so can retard the subsequent dissolution of the metal. Since, HCl is more and rapidly ionizable than H₂SO₄, the inhibition efficiency in 5% HCl medium more than that in 5% H₂SO₄.

From all these facts, we can conclude that the natural water extract of DP enhanced the corrosion of steel dissolution in acid solution due to containing large amounts of organic substances composed of steriodes, flavonoids, tannins, that contains several functional groups like OH, N, O,etc which improve the corrosion inhibition through synergistic effect.

CONCLUSIONS

The tested inhibitor (DP) exhibited as acid corrosion inhibitor with inhibition efficiency 87 % and 72 % in 5 % HCl and 5 % H₂SO₄ respectively, which are more or less equal when compared to the inhibition efficiency of some green compounds.

The inhibitor has a higher good performance at room temperature where the inhibition efficiency decreases with raising the temperature from 30 to 60°C.

The appearance of the surface of the mild steel specimens after treatment with the inhibited acids at room temperature revealed no significant local attack.

The test inhibitor is commercially available, non-toxic and it is eco-friendly in nature so recommended to be used in mild steel dissolution process and cooling water systems.

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The adsorption of this inhibitor on mild steel surface obeys Langmuir's adsorption isotherm.

The inhibitor showed predominantly cathodic behavior in 5% HCL acid and acted as anodic inhibitor in 5% H₂SO₄ acid medium.

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