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Inhibition of mild steel corrosion in HCl using pineapple leaves (*Ananas comosus L.*) extract

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Abstract The corrosion inhibition of mild steel in HCl by pineapple leaves extract was studied using weight loss and hydrogen evolution methods at 30–60 °C. It was found that the pineapple leaves extract inhibited the acid induced corrosion of mild steel. The inhibition efficiency increases with increase in the extract concentration and with rise in temperature. Adsorption of the extract was found to obey Langmuir adsorption isotherm at all the concentrations and temperatures studied. The mechanism of chemical adsorption is proposed from the trend of inhibition efficiency with temperature. The proposed mechanism was also corroborated by kinetic and thermodynamic parameters obtained.

Introduction

Acidization of petroleum oil wells is one of the most important stimulation techniques for oil exploration. It is brought about by using a solution of 15–28% hydrochloric acid (HCl). In order to reduce the aggressive attacks of acid on tubing and casting materials, inhibitors are usually incorporated to acid solution during acidization process. Available literature on high temperature acid corrosion inhibition has shown that effective corrosion inhibitors during acidization include acetylenic alcohol, alkenyl phenones, aromatic aldehydes, nitrogen-containing heterocyclic and their quaternary salts and condensation products of carbonyls and amines [1–7].

Although synthetic organic compounds [8–10] have proved to be effective in inhibiting the corrosion of metals in HCl corrosive environment, the high cost and toxic nature of some of the compounds have been seen as a major setback. The need to develop economical, non-toxic, readily available as well as environmentally friendly processes to fill this gap has now made researchers to focus on the use of natural products and plant extracts as corrosion inhibitors

The use of plant extracts (green corrosion inhibitors) as eco-friendly corrosion inhibitors is of great interest from an environmental perspective and is attracting a significant level of attention [11].Green corrosion inhibitors are natural organic compounds that are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Most green corrosion inhibitors are obtained from ethanol, aqueous acid, methanol or formaldehyde extracts of plant materials. They are biodegradable and do not contain heavy metals or other toxic compounds. Various reports have highlighted the successful application of plant extracts as corrosion inhibitors of metals and their alloys. Oguzie [12] reported on the efficacy of *Telfaria occidentalis,Occimum viridis, Azadirachta indica, Hibiscus sabdariffa* leaf extracts as well as the seeds of *Garicina kola* as corrosion inhibitors for mild steel in 2 M HCl and 1 M H_2SO_4. Noor [13] studied the temperature effects on mild steel corrosion in 2 M HCl and H_2SO_4 in the absence and presence of aqueous extract of *Fenugreek* leaves (AEFL). The inhibitive action of leaves (LV), seeds (SD) and a combination of leaves and seeds (LVSD) extracts of *Phyllanthus amarus* on mild steel corrosion in HCl and H_2SO_4 solutions was studied by Okafor et al. [14]. The extract of hena and its constituents as corrosion inhibitors of mild steel in hydrochloric acid has also been reported by Ostovari et al. [15]. Also reported is the corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by the leaf extract of *Occimum viridis* [11]. Reports by Abdel-Gaber

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et al. [16] on the inhibitive action of extract of chamomile (*Chamaemelum mixtum L.*), halfabar (*Cymbopogon proximus*), black cumin (*Nigella sativa L.*) and kidney bean (*Phaseolus vulgaris L.*) plants, indicate that the solution of the extracts of these plants could serve as an effective inhibitor for corrosion of steel in sulphuric acid media. The corrosion inhibition of mild steel by *Datura metel* in acid medium has been reported by Sethuraman and Raja [17]. Rahim et al. [18] reported on the inhibitive behaviour of mangrove tannins and their flavonoid monomers on steel in acidic medium. The inhibitive effect of lupine extract on the corrosion of steel in hydrochloric and sulphuric acid solutions has also been reported by Abdel-Gaber et al. [19]. El-Etre [20] reported on the inhibitive action of the aqueous extract of olive (*Oleo europaea L*) leaves towards the corrosion of C-steel in 2 M HCl. *Zenthoxylum alatum* plant extract was found to exert inhibitory action on the corrosion of mild steel in 20, 50 and 88% aqueous orthophosphoric acid [21]. El-Etre and El-Tantawy [22] investigated the inhibitive action of extract of *Ficus nitida* leaves on general and pitting corrosion of C-steel, nickel and zinc in different aqueous media. Raja and Sethuraman [23] have given a comprehensive review of natural products as corrosion inhibitors for metals in corrosive media. All the studies so far have shown that the inhibiting action of plants' solution extracts are due to the presence of some phytochemical constituents including tannins, organic and amino acids, alkaloids and pigments. Earlier reports in our laboratory also showed that gum Arabic and *Raphia hookeri* exudates gum functioned as corrosion inhibitor for mild steel in acidic environment [24, 25].

Pineapple has long been recognized as one of the most popular tropical and subtropical fruits. It is grown extensively in Hawaii, Philippines, Caribbean area, Malaysia, Taiwan, Thailand, Australia, Mexico, Kenya, South Africa and Hainan province of China [26]. Apart from the pineapple fruits being used for nutritional food, some folk medicinal uses were found. In Thailand, pineapple leaves were used as an indigenous medicinal plant for the treatment of dysuria [27]. In China, its cortexes served as alexiphamic, antitussive and antidiarrhea agents, and the leaves were usually used as antidyspepsia or antidiarrhea agents in Chinese Traditional Medicine [26].

The efficiency of organic compounds including plant extracts as corrosion inhibitors is influenced by several factors such as pH, temperature, metal type, solution composition as well as concentration of the plant extracts. Previous studies [28] in our laboratory showed that pineapple leaves extract is an effective corrosion inhibitor for aluminium in 0.1 M HCl solution with the highest inhibition efficiency of 96.09% obtained at extracts concentration 0.5 g/L at 60 °C. There has been no report to our knowledge on the corrosion inhibition of mild steel in acid media using pineapple leaves extract as inhibitor. We, therefore, present in this article the corrosion inhibition of mild steel in 1 M HCl using pineapple leaves extract investigated at 30–60 °C using weight loss and hydrogen evolution methods as part of our contribution to the growing interest on environmentally friendly corrosion inhibitors.

Experimental

Materials preparation

Mild steel sheets of composition Mn 0.6%, C 0.15%, P 0.03%, and remaining Fe were used in the study. Each sheet of 0.046 cm thickness was mechanically pressed cut into coupons of dimensions 5 cm × 4 cm (for weight loss studies) and 3 cm × 3 cm × 0.046 cm (for hydrogen evolution studies). The coupons were used as cut, but they were degreased in absolute ethanol, dried in acetone and stored in a moisture-free dessicator prior to use in corrosion studies. The corrosive medium was 1 M HCl prepared from 37% analytical grade supplied by Sigma-Aldrich. Deionised water was used for the preparation of all reagents. Pineapple leaves were obtained from Ekpene Obom village in Etinan local Government Area of Akwa Ibom State, Nigeria.

Preparation of the extract of pineapple leaves

Pineapple leaves were sun dried and ground to powder using a manual blender. One kilogramme of the dry powered sample was extracted using absolute ethanol for 48 h. The extract was concentrated initially using vacuum evaporator and finally by evaporation to dryness on a steam bath to obtain a solid residue devoid of ethanol. From the solid residue, different concentrations was prepared by weighing 0.1–0.5 g and then dissolved in one litre of 1 M HCl solution for weight loss and hydrogen evolution measurements.

Weight loss measurements

The procedure followed for weight loss was similar to that reported earlier [11, 14, 24, 25]. The progress of the corrosion reaction was monitored by determining the weight loss of the coupons (obtained as the differences in the weight of the coupons after immersion in different solutions of the system and original weight of the coupons). The tests were performed in triplicate to guarantee the reliability of the results, and the mean value of the weight loss is reported. The reproducibility of the experiment was higher than 95%. From the weight loss values, corrosion rates were computed using the expression:

$$\upsilon = \frac{\Delta W}{At} \quad (1)$$

where υ is the corrosion rate (mg cm^{-2} h^{-1}), ΔW is the weight loss of the mild steel coupon in mg, A is the sectional area of the mild steel coupon in cm^2 and t is the exposure time of the mild steel coupon in h.

The inhibition efficiency of pineapple leaves extract was evaluated from the following equation:

$$\eta\% = \left(\frac{v_0 - v_1}{v_0}\right) \times 100 \quad (2)$$

where υ_0 and υ_1 are the corrosion rates of the mild steel coupons in the absence and presence of inhibitor respectively.

Hydrogen evolution measurements

The technique relies on measurement of the volume of hydrogen gas evolved from the surface of a corroding metal. The measurements was performed using gasometric assembly; its detailed description has been reported elsewhere [29]. The procedure followed was similar to that reported by other authors [28–30]. The test solution was kept at 100 mL. The progress of corrosion in the absence and presence of test inhibitor (plant extract) was monitored by careful measurements of the volume of hydrogen gas evolved at fixed time intervals. The experiment was performed for 1 M HCl (blank) and different concentrations of inhibitor (0.1–0.5 g/L) at 30–60 °C maintained using a thermostated water bath. The inhibition efficiency (η%) was calculated using the equation:

$$\eta\% = \left(1 - \frac{V^1_{\mathrm{H}t}}{V^{\mathrm{o}}_{\mathrm{H}t}}\right) \times 100 \quad (3)$$

where $V^1_{\mathrm{H}t}$ is the volume of hydrogen evolved at time 't' for inhibited solution and $V^{\mathrm{o}}_{\mathrm{H}t}$ is the volume of hydrogen evolved at time 't' for uninhibited solution.

Results and discussion

Weight loss, corrosion rates and inhibition efficiency

The effect of extract of pineapple leaves towards the corrosion inhibition of mild steel in aggressive 1 M HCl was followed using weight loss technique at 30–60 °C. The results obtained are presented in Fig. 1 and Table 1. Figure 1 shows the variation of weight loss against time for mild steel corrosion in 1 M HCl without and with different concentrations (0.1–0.5 g/L) of the extract at 30, 40, 50 and 60 °C. From the figure, it is clear that weight loss of mild steel was reduced in the presence of the extract compared to its absence. Inspection of the figure also revealed that weight loss of mild steel increases with increase in temperature as well as immersion time both in the absence and presence of the extract. The extent of weight loss in the presence of the extract was found to be concentration dependent, decreasing as concentration of the extract increased.

Table 1 shows the corrosion rates of mild steel coupon in 1 M HCl in the absence and presence of different concentrations of pineapple leaves extract at different temperatures. As observed from the table, a remarkable decrease in mild steel corrosion rate was obtained in the presence of the extract compared with the ones in the blank solution at each temperature under study. Also, corrosion rate decreases with increase in the concentration of the extract but rises with increasing temperature both in the inhibited and uninhibited acid solutions. Decrease in corrosion rate of mild steel on introduction of the extract to the corrosive medium is an indication that the extract is exerting inhibitive effect and retarding the acid-induced corrosion of mild steel coupons. The effectiveness of the extract in retarding the corrosion of mild steel in 1 M HCl was obtained by comparing the corrosion rates of the mild steel in the presence of the extract and in the blank acid solution and expressed in terms of the inhibition efficiency (η%). The inhibition efficiency values are listed in Table 1. Results in the table show that inhibition efficiency increases as the concentration of the extract increases reaching a maximum value at the higher concentration (0.5 g/L) of the extract studied. Inhibition efficiency also increases with increase in temperature. Similar results involving plant extracts used as corrosion inhibitor for mild steel in acid media has been reported in the literature [13, 14, 31–33]. It has been pointed out that the increase in inhibition efficiency with increase in extract concentration is an indication of an increase in the number of components of the extract adsorbed over the mild steel surface blocking the active sites, in which direct acid attacks proceed and protect the metal from corrosion, while the increase in inhibition efficiency with temperature rise is suggestive of strong adsorption of the phytoconstituents of the extract on the mild steel surface forming a protective layer and shielding the metal from corrosion [32, 33].

It is a common knowledge that corrosion inhibition action is afforded by the adsorption of the components of the extract onto the metal surface. Studies by some research groups have also shown that the ethanolic extract of pineapple leaves is composed of ananasate, 1-O-caffeoylglycerol, 1-O-p-coumaroylglycerol, caffeic acid, p-coumaric acid, β-sitosterol, and daucosterol [34, 35]. It is, therefore, pertinent to say that the adsorption of these compounds onto mild steel surface is responsible for corrosion inhibition

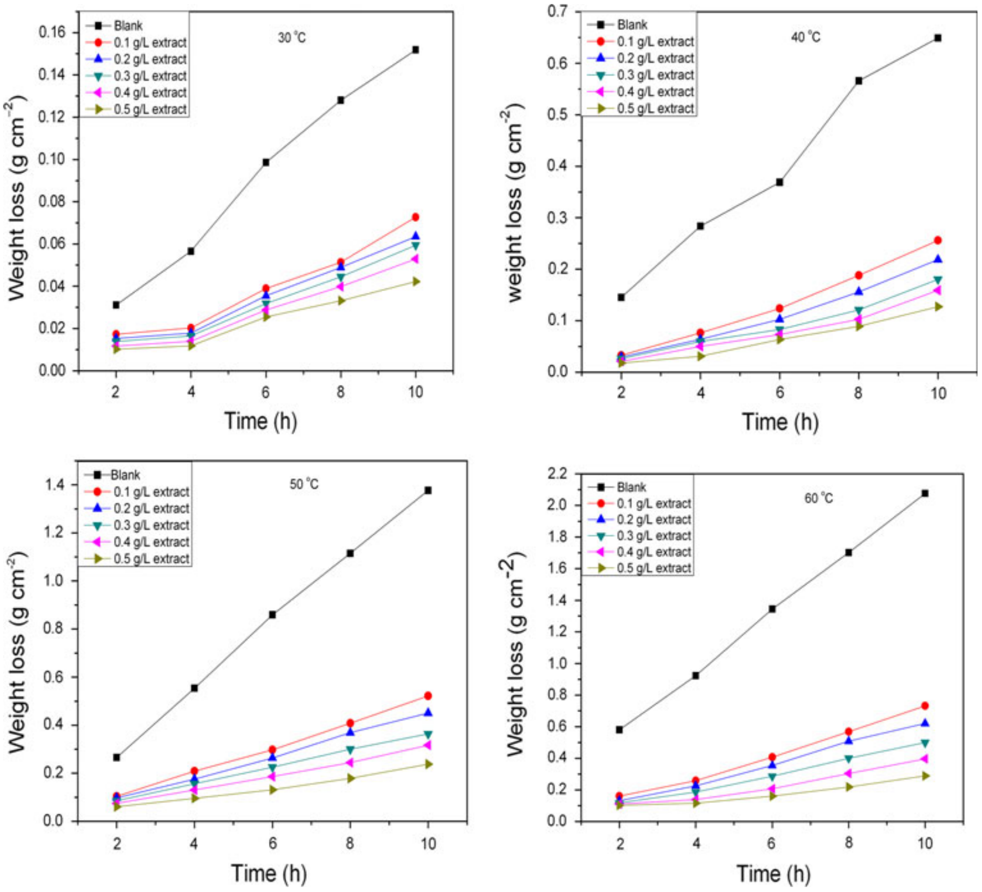

Fig. 1 Variation of weight loss against time for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of extract at 30, 40, 50 and 60 °C

Table 1 Calculated values of corrosion rates and inhibition efficiency for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of extracts at different temperatures from weight loss measurement

Systems/concentration	Corrosion rate (mg cm^{-2} h^{-1})				Inhibition efficiency (η%)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
1 M HCl (blank)	0.76	3.25	6.89	10.4	–	–	–	–
0.1 g/L extract	0.36	1.28	2.60	3.66	52	54	62	65
0.2 g/L extract	0.32	1.09	2.30	3.10	58	61	67	70
0.3 g/L extract	0.30	0.90	1.80	2.50	61	66	73	76
0.4 g/L extract	0.26	0.79	1.60	2.00	65	76	77	81
0.5 g/L extract	0.21	0.64	1.20	1.40	72	81	83	86

effect. One of the main criticisms of the use of plant extract as corrosion inhibitors is the inability to pinpoint the major active component that is responsible for the inhibiting action owing to the complex chemical composition of the crude extract. However, further investigation and the use of surface analytical techniques will enable the characterization of the active materials in the adsorbed layer, and assist in identifying the most active ingredients in the extract of pineapples leaves which is currently being pursued in our laboratory.

A clarification of mechanism of inhibition requires some knowledge of interaction between the protective compound and the metal surface. In HCl solution, specific adsorption of chloride ions renders the surface of mild steel negatively charged and susceptible to adsorption of cationic moieties of the extract component. The joint adsorption of the anion with cation results in a positive synergistic effect which could possibly account for the observed increase in inhibition efficiency even at low extract concentration. In addition, the co-adsorption of the components of the pineapple leaves extract and the intermediates on the metal surface may lead to the formation of metal–inhibitor complex. The resulting complex could either catalyze or inhibit further metal dissolution depending on its relative solubility. From the observed results, it can be inferred that the insoluble Fe–inhibitor complex dominates the adsorbed intermediates and thus the resultant inhibitive effects even at low extract concentration.

Hydrogen evolution measurements

The corrosion of mild steel in 1 M HCl in the absence and presence of pineapple leaves extract was also investigated at 30–60 °C using hydrogen evolution method. The results obtained from this technique are presented in Fig. 2 and Table 2. Figure 2 shows the plot of volume of H_2 evolved with immersion time at 30, 40, 50 and 60 °C. Inspection of the figure reveals that the volume of hydrogen gas evolved varies linearly with reaction time. The plots also indicate the decreased deflection of H_2 gas evolution on the introduction of the pineapple leaves extract showing that the extract actually afforded corrosion inhibition of mild steel in the acidic environment. The volume of hydrogen gas evolved was observed to increase with increase in temperature in the absence and presence of the leaves extract. Also the volume of H_2 evolved was dependent on extract concentration, decreasing with increasing extract concentration.

The values of hydrogen evolution rate (obtained from the linear portion of the plots in Fig. 2) which can be correlated to the corrosion rate of mild steel coupons in the absence and presence of the extract as well as the inhibition efficiency at different temperatures are given in Table 2. From the table, it is clearly seen that hydrogen evolution rates were reduced in the presence of the extract compared to the blank acid solution. Inspection of the table further reveals that hydrogen evolution rate of mild steel in the presence of the extract decreases with increase in concentration but increases with temperature rise. Results presented in Table 2 also show that inhibition efficiency increases with increase in the concentration of the extract and also with increase in temperature. Increase in inhibition efficiency with increase in temperature is suggestive of chemical adsorption of the pineapple leaves extract components onto the mild steel surface. It is worthy to mention that inhibition efficiency obtained from the hydrogen evolution method follow the same trend observed from the weight loss method and results from the two independent methods were in good agreement.

Fig. 2 Variation of volume of H_2 evolved with time for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of extract at 30, 40, 50 and 60 °C

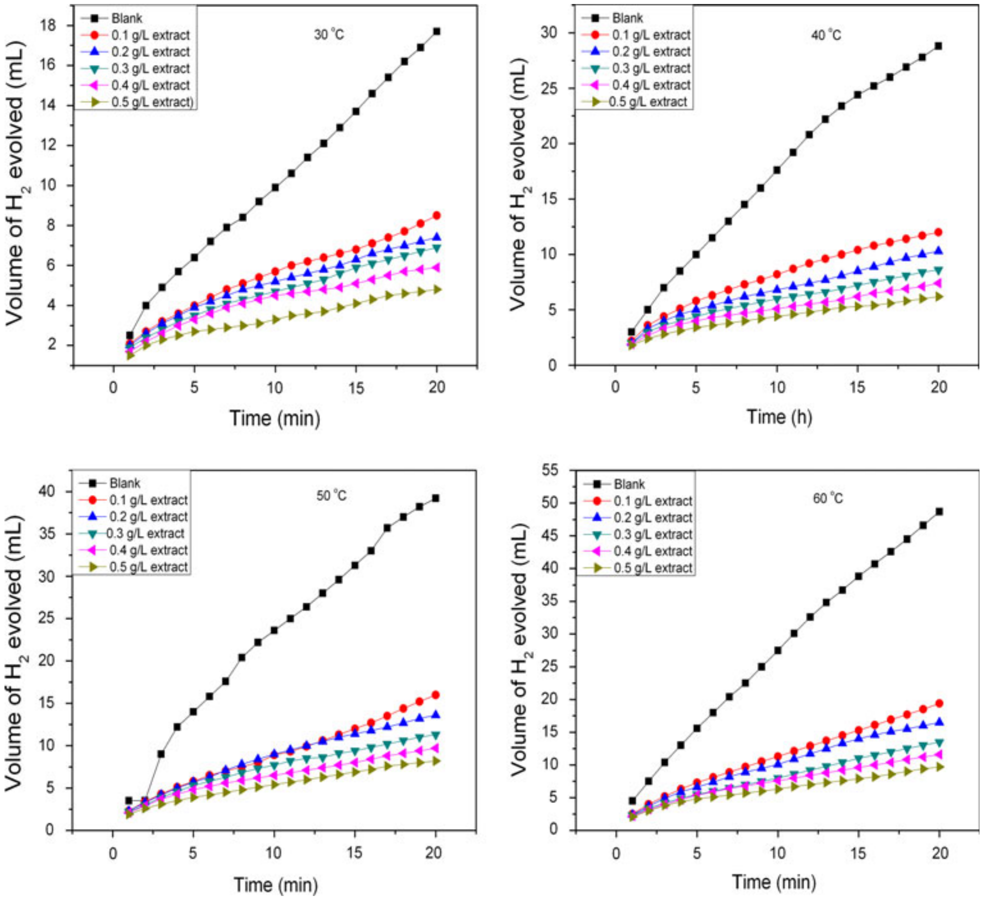

Table 2 Calculated values of H_2 evolution rates and inhibition efficiency for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of extracts at different temperatures from hydrogen evolution measurement

Systems/concentration	Hydrogen evolution rate (mL min^{-1})				Inhibition efficiency (η%)			
	30 °C	40 °C	50 °C	60 °C	30 °C	40 °C	50 °C	60 °C
1 M HCl (blank)	0.89	1.44	1.96	2.44	–	–	–	–
0.1 g/L extract	0.43	0.60	0.80	0.97	52	58	59	60
0.2 g/L extract	0.37	0.52	0.68	0.83	58	64	65	66
0.3 g/L extract	0.35	0.43	0.57	0.68	61	70	71	72
0.4 g/L extract	0.30	0.37	0.49	0.58	67	74	75	76
0.5 g/L extract	0.24	0.31	0.41	0.49	73	78	79	80

Adsorption considerations

The increase in efficiency of inhibition by pineapple leaves extract determined by weight loss and hydrogen evolution methods with increase in the extract concentration indicates that the extract are adsorbed at the mild steel surface at higher concentration leading to greater surface coverage. Figure 3 illustrates the relationship between the surface coverage and concentration from the two techniques employed at 30 and 60 °C. The surface coverage was evaluated from the expression: $\eta\% = \theta \times 100$; assuming a direct relationship between inhibition efficiency (η%) and surface coverage (θ). The plot reveals linear relation between surface coverage and extract concentration at both temperatures which implies that more components of the extract were adsorbed on the metal surface as the concentration increases. In order to clarify the nature of adsorption, theoretical fitting of the surface coverage values to different isotherms were undertaken and the value of correlation coefficient (R^2) was used to determine the best fit isotherm. Langmuir adsorption isotherm was found to be the best fit. Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \qquad (4)$$

where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process.

The plot of C/θ against C is shown to be linear in Fig. 4. The slopes of the linear plots were 1.28, 1.04, 1.10 and 1.06 at 30, 40, 50 and 60 °C, respectively, and R^2 at all temperatures being 0.99. The values of the slopes at 40–60 °C indicate that the adsorption of the extract on steel surface obeys well the isotherm. The considerable deviation of the slope from unity observed at 30 °C may be explained on the basis of the interaction among the adsorbed species on the surface of the metal. Given the complex composition of the extract, the different components can be adsorbed on the cathodic and anodic sites of the metal surface, and such adsorbed species may interact by mutual repulsion or attraction. It is, therefore, pertinent to say that the adsorption of the extract on the steel surface at this temperature can be more appropriately represented by a modified Langmuir equation suggested by Villamil et al. [36] taking into consideration the interactions between adsorbate species as well

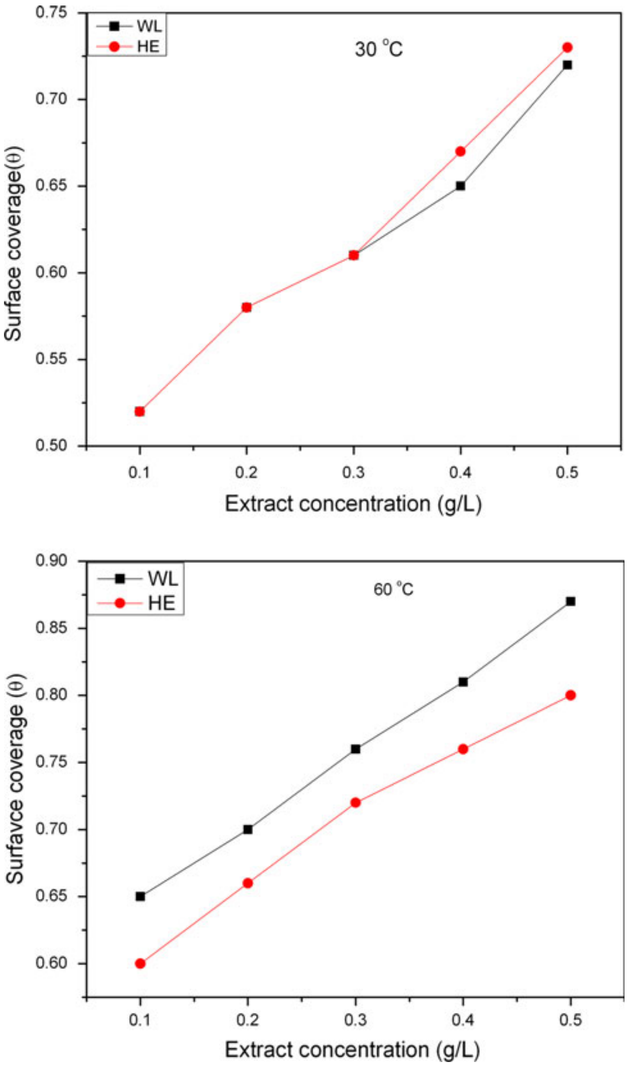

Fig. 3 Adsorption curve for pineapple leaves extract on mild steel in 1 M HCl from weight loss and hydrogen evolution techniques at 30 and 60 °C

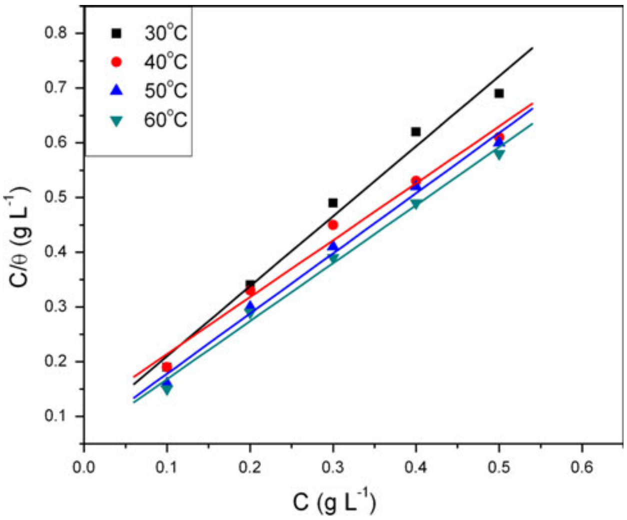

Fig. 4 Langmuir adsorption isotherm model for mild steel in 1 M HCl containing pineapple leaves extract at different temperatures

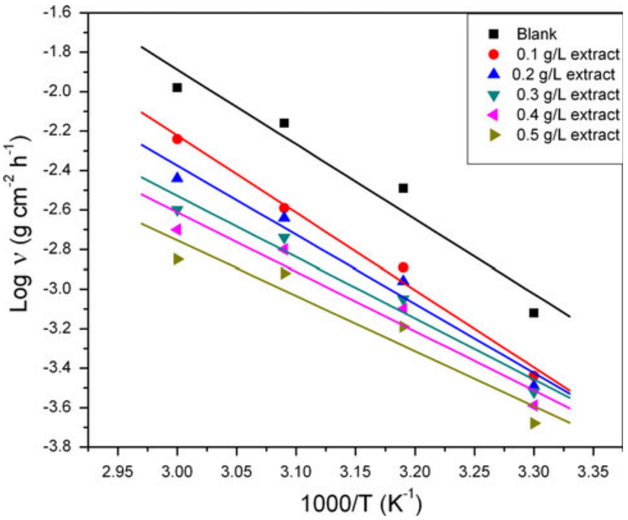

Fig. 5 Arrhenius plot for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of pineapple leaves extract

as changes in heat of adsorption with changing surface coverage as follows:

$$\frac{C}{\theta} = \frac{n}{K_{\text{ads}}} + nC \qquad (5)$$

Kinetics and thermodynamics considerations

Temperature has great effect on the corrosion phenomenon. In general, the corrosion rate increases with rise in temperature. In this study, the effect of temperature on the corrosion and inhibition process of mild steel in 1 M HCl in the absence and presence of different concentrations of the extract after 10 h of immersion was followed at 30–60 °C using weight loss measurements. The result of the effect of temperature on corrosion rate as presented in Table 1 is in agreement with earlier reports [33–35], increasing as temperature increases. The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation:

$$v = A[\exp(-E_a/RT] \qquad (6)$$

where υ is the corrosion rate, E_a is the apparent activation energy of the mild steel dissolution, R is the molar gas constant, T is the absolute temperature, and A is the frequency factor Figure 5 depicts Arrhenius plot as log of corrosion rate (log υ) against the reciprocal of temperature ($1/T$) for mild steel in 1 M HCl in the free acid solution and the acid containing different concentrations of pineapple leaves extract. The plots obtained are straight lines and the activation energy was evaluated from the slope of the straight line plots. The calculated values of activation energy are listed in Table 3. It can be seen in the table that E_a is lower in the presence of the inhibitor than in the absence of the inhibitor. This observation further supports the proposed chemisorption mechanism because unchanged or lower E_a in inhibited systems compared to blank has been reported [35, 37] to be indicative of chemical adsorption mechanism whereas increased E_a suggests a physical adsorption mechanism. Further inspection of Table 3 also revealed that E_a monotonously decreases with increase in extract concentration with the lowest value (52.5 kJ mol^{-1}) being obtained at the highest extract concentration (0.5 g/L) studied. Similar observation has been reported by Noor [13] in his study of temperature effects on the corrosion inhibition of mild steel in acidic solutions by aqueous extract of Fenugreek leaves.

Further insight into the adsorption mechanism is offered by considering the thermodynamic functions for the mild

Table 3 Activation parameters for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of pineapple leaves extract

Systems/concentration	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	ΔH* (kJ mol^{-1})	ΔS* (J mol^{-1} K^{-1})
1 M HCl (blank)	72.5	–	69.3	−77.4
0.1 g/L extract	63.6	16.2	61.1	−86.9
0.2 g/L extract	62.8	15.5	60.1	−88.4
0.3 g/L extract	58.6	19.6	55.9	−90.9
0.4 g/L extract	56.7	19.6	54.0	−92.7
0.5 g/L extract	52.5	23.0	49.8	−95.9

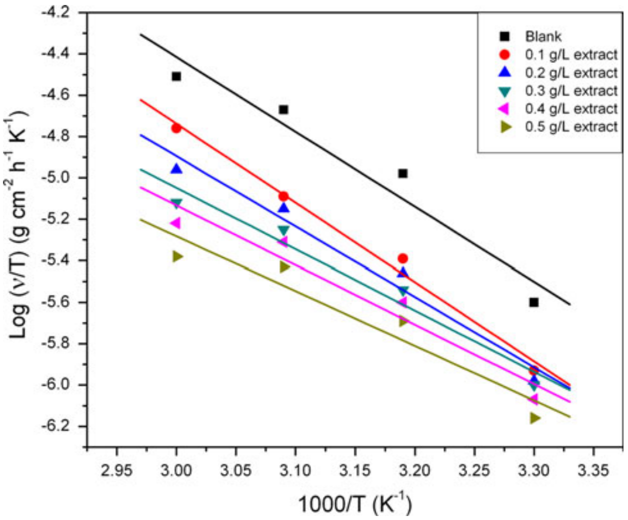

Fig. 6 Transition state plot for mild steel corrosion in1 M HCl in the absence and presence of different concentrations of pineapple leaves extract

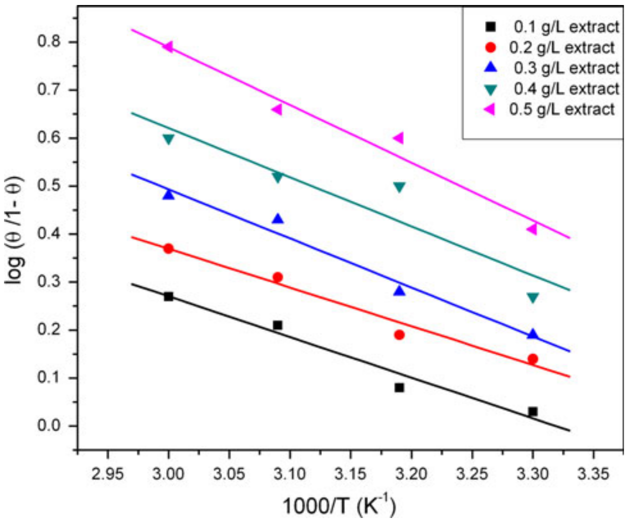

Fig. 7 Plot of log ($\theta/1 - \theta$) against 1/T at different concentrations of pineapple leaves extract

steel dissolution in 1 M HCl in the absence and presence of various concentrations of pineapple leaves extract (Fig. 6). In this regards, Transition state equation was used to evaluate the corrosion activation parameters, namely, the enthalpy of activation (ΔH^*) and entropy of activation (ΔS^*). Transition state equation is given by the expression:

$$v = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (7)$$

where υ is the corrosion rate, h is the Planck's constant, N is the Avogadro's number, R is the universal gas constant and T is the absolute temperature. The plots of log (υ/T) against $1/T$ for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of extract are presented in Fig. 6. Linear plots were obtained with slope of ($-\Delta H^*/2.303R$) and an intercept of [log (R/Nh) + ($\Delta S^*/2.303R$)] from which the values of ΔH^* and ΔS^*, respectively, were computed and listed in Table 3. It is seen from the table that ΔH^* varies in the same manner as E_a but the values of ΔH^* were lower in comparison to that of E_a. The lower ΔH^* values compared to E_a has been reported [13] to indicate that the corrosion process must involved a gaseous reaction, simply hydrogen evolution reaction associated with decrease in total reaction volume. It is found that for all systems, the average value of the difference $E_a - \Delta H^*$ is in the range 3.2–2.7 kJ mol^{-1} which is very close to the approximate value estimated for RT (2.69 kJ mol^{-1}); where T is in the range of experimental temperatures. Noor [13] has reported the average value of 2.67 kJ mol^{-1} as the difference between E_a and ΔH^* in his studies involving Fenugreek leaves in HCl and H_2SO_4 solutions. This result indicates that the corrosion process is a unimolecular reaction characterized by the following equation [13, 38]:

$$E_a - \Delta H^* = RT \quad (8)$$

Positive sign of the enthalpies reflects the endothermic nature of the steel dissolution. The values of entropy of activation (ΔS^*) in the absence and presence of the extract are negative (Table 3). This indicates that the activated complex in the rate determining step represents an association rather than dissolution meaning that a decrease in disordering takes place on going from reactants to activated complex [39, 40]. Also the ΔS^* tends to more negative values showing more ordered behaviour as the extract concentration increases leading to increase inhibition efficiency.

The values of the heat of adsorption were evaluated from the kinetic thermodynamic model [41, 42]:

$$\left[\frac{\theta}{1-\theta}\right] = AC\exp(-Q_{\text{ads}}/RT) \quad (9)$$

where A is a constant, C is the inhibitor concentration, θ is the occupied and ($1 - \theta$) is the vacant site not occupied by the inhibitor. Figure 7 depicts the plot of log [$\theta/(1 - \theta)$] as a function of $1/T$ for the different concentrations of the extract. The values of heat of adsorption were estimated from the slope of the linear plots and are listed in Table 3. The values are positive and increases with increase in concentration of the extract. Positive values of Q_{ads} (as obtained in this study) has been reported to indicate that the inhibitor adsorption and, hence, inhibition efficiency increases with rise in temperature, while negative values means the opposite effect [42]. The positive values of heat of adsorption obtained also support the chemical adsorption mechanism proposed.

Conclusions

Results obtained from the two methods employed revealed that the extract of pineapple leaves is an effective inhibitor for mild steel corrosion in 1 M HCl. The inhibition efficiency of the extract increases with increase in the extract concentration and also with increase in temperature. The adsorption of the extract on mild steel surface in an acidic medium follows Langmuir adsorption isotherm. The phenomenon of chemical adsorption is proposed from the trend of increase in inhibition efficiency with increase in temperature. The inhibition efficiencies obtained by weight loss and hydrogen evolution methods are in reasonably good agreement. The inhibition mechanism was further corroborated by the values of activation parameters obtained from the experimental data.

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