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Full Length Research

Cnestis ferruginea as eco-friendly corrosion inhibitor of mild steel in corrosive environment

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***Cnestis ferruginea* leaves extract was studied as corrosion inhibitor for mild steel in 1MHCl at temperatures 30^0C and 45^0C using gravimetric and gasometric techniques. *C. ferruginea* leaves extract was found to inhibit corrosion of mild steel in acid medium. The inhibition efficiency increased as concentration of *C. ferruginea* extract increased but decreased with rise in temperature suggesting physical adsorption of the extract on mild steel surface. The calculated values of apparent activation energy, free energy of adsorption and heat of adsorption confirmed the physisorption mechanism. The inhibitor adsorption characteristics were approximated by the Langmuir isotherm.**

Keywords: *Cnestis ferruginea,* eco-friendly inhibitor, gasometric techniques, mild steel

INTRODUCTION

Due to the excellent mechanical properties and low cost, mild steel is extensively used as a constructional material in many industries. However when this mild steel is exposed to the corrosive industrial environment, it easily corrodes. Normally acid solutions such as hydrochloric acid are widely used in areas like acid pickling, industrial cleaning, oil well cleaning etc. The use of these acid solutions poises danger for mild steel applications. To savage the situation inhibitors are being introduced to help protect the mild steel and save the industries the resources that would have been wasted on repair and maintenance. Regrettably some of these synthesized corrosion inhibitors are toxic and therefore hazardous to the environment. The current growing trend towards bio-technology has led many researchers to discover green inhibitors of plant source which are environmental friendly, ecologically acceptable and sustainable. (2-17).

The results from those researches have proved that plant extracts can be used as effective corrosion inhibitors of mild steel in acid media. However it is stated in (1) that the corrosion inhibition properties in many plants extracts is due to their heterocyclic constituents like alkaloids, flavonoids, tannins etc. Secondly there is a suggestion that medicinal plants exhibit good corrosion inhibiting properties, it has been found that their compounds contains hetero atoms such as N, S, O, and P which are reported to have corrosion inhibiting properties. (3-8). This spurs our interest and suggestion that *Cnestis ferruginea* plant will possess good inhibition properties since it has good medicinal values and contains phytochemicals. *Cnestis ferruginea* plant is a shrub or tree growing to about 6 metres tall. It is of a great medicinal value within African society. The root is being used to treat skin infections and can be applied as ointment, which can be used against sarcina lutca and staphylococcus aureus (19). The leaf is rubbed onto the body in the treatment of fever. The whole pulped plant is used for treating all manners of asthenia. The fruit can be taken as tonic and is being used to treat bronchial infections especially whooping-cough and tuberculosis. *Cnestis ferruginea* contains phytochemicals like alkaloids flavonoids, tannins, ceumarins, cylocosides, polysaccharides, phenols, terpenes and terpenoids (20), it is also stated in (18) that *Cnestis ferruginea* contains antraquilous, quinolizidine and tannin and can be used as bioactive male anti-fertility. Owing to these phytochemical constituents of *Cnestis ferruginea* and its medicinal properties, we suggest that it will possess good corrosion inhibition properties. This study investigates the inhibitory effects of *Cnestis ferruginea* leaves extracts on corrosion of mild steel in 1M HCl solution.

MATERIALS AND METHOD

Material preparation: Material used for the study was mild steel sheet of composition (wt %) Mn (0.6), P (0.36) C (0.15) and Si (0.03) the rest being Fe. The sheet was mechanically pressed cut to form different coupons, each of dimension 3 x 3 x 0.1cm.

Each coupon was degreased by washing with ethanol dried in acetone and preserved in a desiccator prior to use. All reagents used for the study were analar grade, and double distilled water was used for their preparation.

Extraction of plant: sample of *Cnestics ferruginea* leaves was dried and pulverized to powder form. 30g of the powdered sample was soaked in a solution of ethanol for 72hrs. The soaked sample was then filtered after 72hrs. The stock solution the extract so obtained was used in preparing different concentrations of the extract in 200mgl^{-1}, 400mgl^{-1}, 600mgl^{-1} and 800mgl^{-1} respectively in 1MHCl solution.

GASOMETRIC METHOD

Gasometric analysis was carried out at 303 and 318K for 3hr as reported in (8,9 and 10). From the volume of hydrogen gas evolved other parameters like degree of surface coverage (θ) and inhibition efficiency (IE) were calculated using equation 1 and 2.

$\theta = (1 - \frac{V_{Ht}^{t}}{V_{Ht}^{0}})$ --1

$IE\ (\%) = (1 - \frac{V_{Ht}^{t}}{V_{Ht}^{0}}) \times 100$ ---------------------------------------2

Where V^{t}_{Ht} is the volume of hydrogen gas evolved at time for inhibited solutions and V^{0}_{Ht} is the volume of hydrogen gas evolved in uninhibited solution.

GRAVIMETRIC ANALYSIS

Weight loss experiment was conducted under total immersion condition in 250ml of test solution at 303 and 318k respectively for 3 hrs.

The test coupons which were weighed before immersion were retrieved at the end of 3hrs, scrubbed with bristle brush under running water until clean. The clean test coupons were dried in acetone and reweighed. The weight loss was taken as the difference between the weight of coupon before and after immersion. With the weight loss data corrosion rate was calculated using equation 3.

$CR = \frac{\Delta Wt}{AT}$ ---3

Where CR is the corrosion rate, A is the surface area of the coupon, T being time of immersion and Wt the weight loss.

RESULTS AND DISCUSSION

The gravimetric analysis of mild steel coupon in 1M HCl solution in the absence and in the solutions containing different concentrations at *Cnestic ferruginea* leaves extract studied is represented graphically in figure 1 and 2. Figure 1 shows a plot of corrosion rate of mild steel

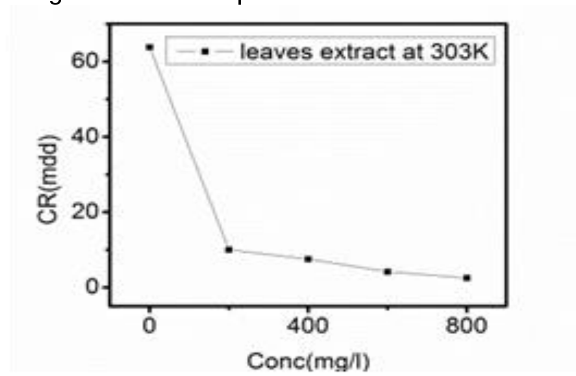

Figure 1: Gravimetrically determined CR against conc. at 303K.

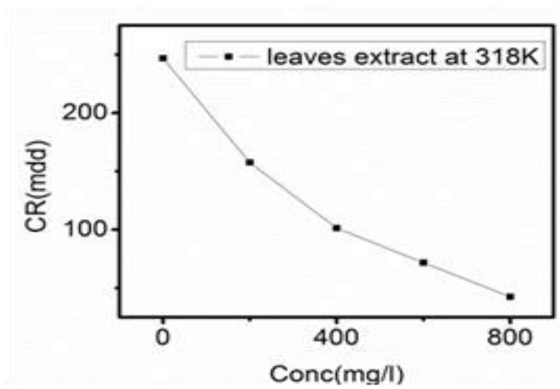

Figure 2: Gravimetrically determined CR against conc. at 318K.

coupon in acidic solution studied against various concentrations of *Cnestic ferruginea* leaves extract at 303K. The result shows that corrosion rate reduced in presence of the plant extract and this effect becomes more pronounced with increasing *C. ferruginea* leave extract concentration. Figure 2 shows graphical representation of corrosion rate against inhibitor concentration at 318K. The result here too show a reduction in corrosion rate in inhibited system compared to the blank system, and it reduced as it did at 303K as concentration increases. The inhibition efficiencies of each concentration of the *Cnestis ferruginea* leaves extract was calculated by comparing the corrosion rate in the absence and presence of *Cnestics ferruginea* leaves extract using the relationship in equation 4 (3).

$IE\ (\%) = (1 - \frac{CR_{in}}{CR_{bl}}) \times 100$ --------------------------------------4

Where IE is inhibition efficiency CR_{in} is corrosion rate in inhibited system and CR_{bl} being the corrosion rate in uninhibited system.

Figure 3 shows plots of inhibition efficiency against concentrations of the leave extract of C. ferruginea in 1M

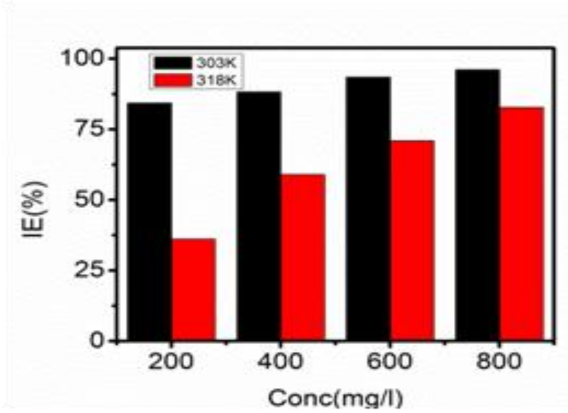

Figure 3: Gravimetrically determined IE against conc.

HCl, at 303 and 318K respectively.

Observations from the figure show increase in inhibition efficiency as the extract concentration increases both at 303 and 318K respectively. A close observation from the figure shows that inhibition efficiency reduced as temperature increased.

Gasometrically determined corrosion rate for mild steel coupons in 1M HCl with the different concentrations of *C.ferruginea* leaves extract at 303 and 318K respectively are depicted in figures 4 and 5. Observations from the

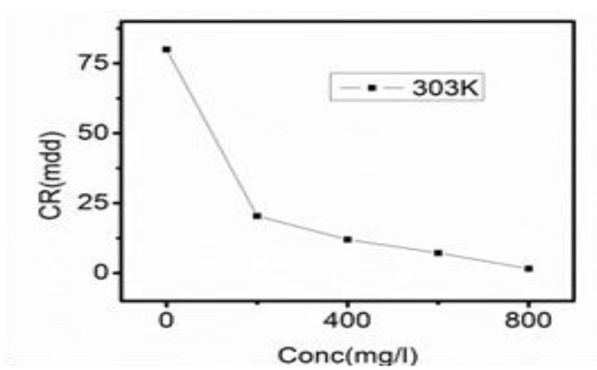

Figure 4: Gasometrically determined CR against conc. at 303K.

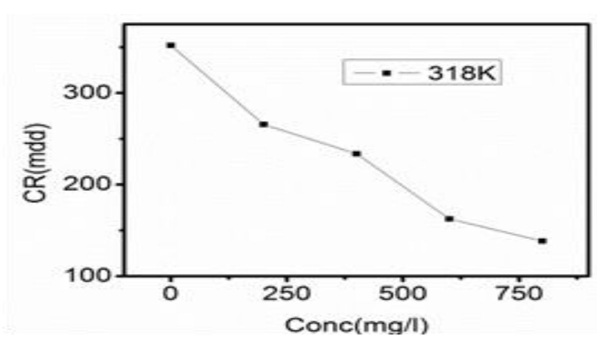

Figure 5: Gasometrically determined CR against conc. at 318K

figures indicate reduction in corrosion rate in leaves extract of *Cnestis ferruginea* both at 303 and 318K when compared with blank system.

A close observation shows that corrosion rate was more pronounced at higher temperature of 318K than it is at 303K. The inhibition efficiencies of each concentration of *Cnestis ferruginea* leaves extract studied gasometrically at 303 and 318K are shown in figure 6. The results show that inhibition efficiency increases as concentration of the extract increases. The inhibition efficiency is observed to be more susceptible at 303K than it is at 318K.

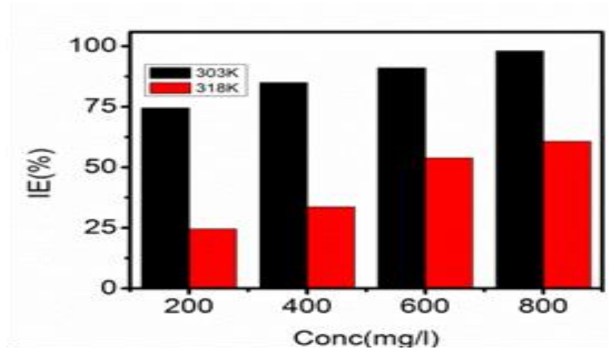

Figure 6: Gasometrically determined I E against conc.

The relationship between the degree at surface coverage (θ) and *C. ferruginea* leaves extract can be represented by the Langmuir adsorption isotherm.

$\frac{C}{\theta}$ = C + $\frac{1}{K_{ad}}$ -- 5

Where C is the concentration of the extract, θ being the degree of surface coverage and K_{ad} is the constant for adsorption and it is related to the free energy of adsorption (ΔG^0_{ad}) by

K = $\frac{1}{55.5}$ exp ($\frac{\Delta G^0_{ad}}{RT}$) --- 6

T is temperature and other parameters maintain their previous meanings. Figures 7 and 8 show the plots of C/θ versus concentration of leaves extract of *C. ferruginea* in 1M HCl at 303 and 318K both gasometrically and gravemetrically studied, to be linear, with intercept 1/K which suggest that the experiment fit languirm adsorption isotherm.

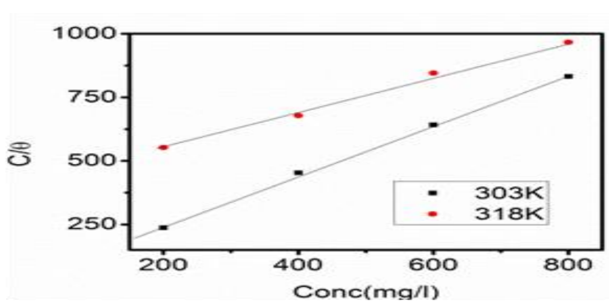

Figure 7: Gravimetrically determined Langmuir Isotherm

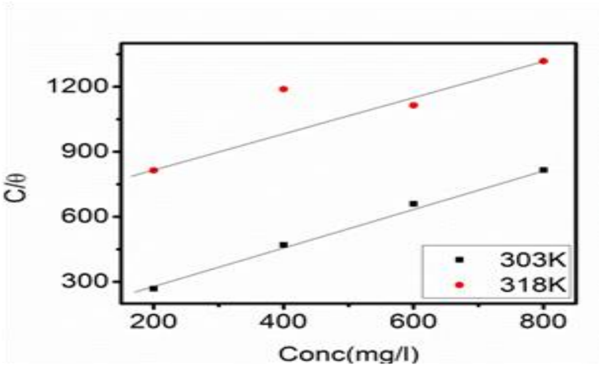

Figure 8: Gasometrically determined Langmuir Isotherm.

The calculated values of ΔG^0_{ad} are shown in table 1 for gravimetically determined and table 2 for gasometrically determined. The negative sings in the values obtained indicates that *C. ferruginea* leaves extract was spontaneously adsorbed to the mild steel surface in acidic medium studied (12).

EFFECT OF TEMPERATURE

Temperature has a significant influence on metal corrosion rates and inhibition efficiencies of corrosion inhibitors when the corrosion reaction involves a cathodic process of hydrogen evolution, the corrosion rate increases exponentially with rise in temperature according to Arrhenius type dependence and the inhibition efficiency decreases as temperature rises. Figure 9 and 10 illustrate the effect of change in temperature on inhibition efficiency of *Cnestis ferruginea*

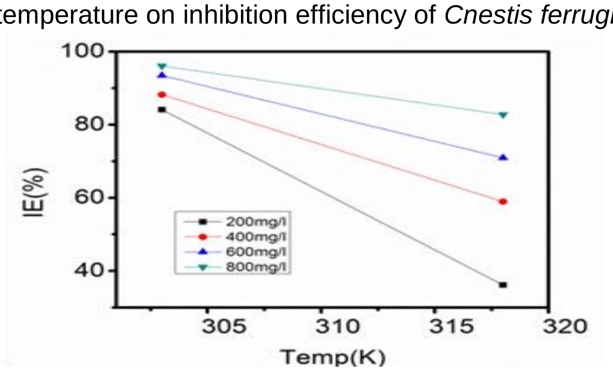

Figure 9: Gravimetrically determined I E against temperature

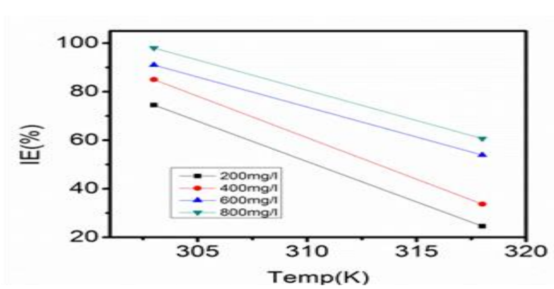

Figure 10: Gasometrically determined I E against temperature

leaves extract on corrosion of mild steel in 1M HCl inhibition efficiencies in all the concentrations studied decreased as temperature increased as temperature both gasometrically studied and grainmetrically studied. This observation can be explained with respect to the characteristic features of the cathodic processes of hydrogen evolution, where the decrease of the reaction with rise in temperature leads to an increase in the rate of the cathodic reaction (13) this effect far overshadows the adsorption and inhibitive effect of *C. ferruginea* because the enhanced rates of hydrogen gas evolution increasingly agitates the interface which hinders inhibitor adsorption and also promotes dispersal of adsorbed inhibitors (12) thus the marked reduction in inhibition efficiency with rise in temperature could be attributed to the shift of the adsorption-desorption equilibrium towards desorption. This behavior suggests that *Cnestis ferruginea* was physically adsorbed on the mild steel surface. (11 and 14). The relation between corrosion rate and temperature is often expressed by the Arrhenius equation

K = A exp (- Ea/RT) ---7

Where Ea is the activation energy, A is the Arrhenius pre-exponential factor and R is the gas constant while T stands for temperature at which the study was conducted. Equation 7 can be further expressed as

$$\text{Log}\left(\frac{CR_2}{CR_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) ----------- 8$$

Where CR_1 and CR_2 are the corrosion rates at temperatures T_1 and T_2 respectively, other parameters retain their previous meanings the apparent activation energies (Ea) for mild steel corrosion in presence and absence of the *Cnestic ferruginea* leave extract were calculated using equation 8 above. The presentation in table 1 for gravimetically determined and table 2 for gasometrical determined, apparent activation energies are observed to increase in inhibited

systems containing leaves extract of *Cnestis ferruginea*. Such behavior coupled with a decrease in inhibition efficiency as temperature increases is evidence of physisorptive interaction between the extract specie and mild steel surface (15, 16 & 17).

Another thermodynamic parameter which further describes the adsorption mechanism operative in the corrosion inhibition process is the heat of adsorption (Q_{ad}). It is related to the surface coverage through the relation in equation 9

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

Where Q_{ad} is heat of adsorption θ_1 and θ_2 are degrees of surface coverage at temperatures T_1 and T_2 respectively. The calculated values of heat of adsorption also shown in table 1 for gravimetically determined and table 2 for gasometrically determined, are all negative, and in the range of – 2. 11 x 10^{-6} to – 2.91 x 10^{-6} Kj mol^{-1} for grvimetrically determined and -2.80X10^{-6} to -4.48X10^{-6} for gasometrically determined in table 2. The negative values of heat at adsorption indicate that adsorption was spontaneous and physical.

Table 1: Presentation of gravimetrically determined apparent activation energy, free energy and heat of adsorption of *Cnestis ferruginea*.

System (mg/l)	Ea (Kj)	ΔG^0_{ad}(Kj) at 303K	ΔG^0_{ad}(Kj) at 318K	Q_{ad} ($Kjmol^{-1}$)
Blank	72.27			
200	147.23	-36.59	-59.36	-2.91×10^{-6}
400	138.97	-40.24	-56.96	-2.14×10^{-6}
600	151.94	-37.81	-55.69	-2.29×10^{-6}
800	151.36	-40.73	-69.54	-2.11×10^{-6}

Table 2: Presentation of gasometrically determined apparent activation energy, free energy and heat of adsorption of *Cnestis ferruginea*.

System (mg/l)	Ea (Kj)	ΔG^0_{ad}(Kj) at 303K	ΔG^0_{ad}(Kj) at 318K	Q_{ad} ($Kjmol^{-1}$)
Blank	79.13			
200	137.07	-42.76	-64.97	-2.84×10^{-6}
400	158.55	-43.07	-67.50	-3.13×10^{-6}
600	166.42	-41.31	-63.16	-2.80×10^{-6}
800	238.20	-28.26	-63.24	-4.48×10^{-6}

CONCLUSION

- Leaves extract of *Cnestis ferruginea* effectively inhibited corrosion of mild steel in 1MHCl solution.
- The inhibitory effect resulted from adsorption of *Cnestis ferruginea* leaves extracts on mild steel surface following Langmuir isotherm.
- Inhibition efficiency of the extract increased with concentration of *C. ferruginea* but decrease with rise in temperature, suggesting physisorption.
- The adsorption mechanism was further confirmed to be physical by examining the values of apparent activation energies and heat of adsorption.

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