ANTICORROSION ACTIVITY OF CACTUS POWDER ON IRON METAL SHEETS

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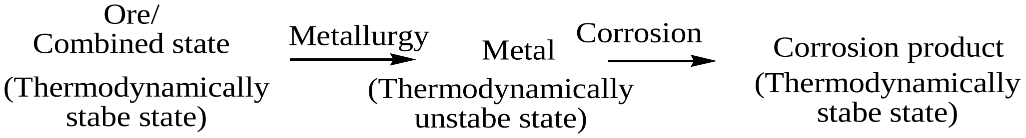
ABSTRACT: *The anticorrosion activity of CE on iron metal sheets was investigated using weight loss method. The result revealed that the rate of corrosion activity is decreased from* $7.887x10^{-3}$ *to* $1.7x10^{-3}$ *mmpy with increasing dose of inhibitors from 0mL to 9mL. But the inhibition efficiency and surface coverage area are increased from 49% to 77% and 0.49 to 0.77, respectively with increasing inhibitor dose from 1mL to 9mL. This is due the fact that as the concentration of inhibitors increased, a larger number of inhibitors molecule is get adsorbed on the metal surface which results more coverage of the corroded metal surface. This makes the metal too difficult from further corrosion by the corrosion agents. In the other hand, the inhibition efficiency and surface coverage area of CE are lower at higher temperature. This is due to the fact that at an elevated temperature desorption of pre-adsorbed inhibitor molecules occur from metal surface; decomposition and rearrangement of some inhibitors may take place which increases corrosion rate at uninhibited metal surface. Adsorption of CE on iron metal sheets are obeyed the Langmuir, Temkin and Frumkin adsorption isotherms. The positive value of activation energy (Ea) and the negative value of free energy of adsorption* ($\Delta G^{o}ad$) *support the physical adsorption of CE iron metal sheets. The large values of the thermodynamic parameters at high dose of CE indicate the stable interaction between CE and iron metal sheets.*

KEYWORDS: Corrosion, Anticorrosion Activities, Metal Sheet, Corrosion Agent, Adsorption and Cactus Extract (CE)

INTRODUCTION

Corrosion is degradation of metals due to interactions with their environments like moistures, acids and oxides [4, 5, 6]. It is mainly for metals, but polymeric, potters and ceramics also undergo degradation by corrosion agents [6]. Many recent studies have been indicated that metals are deteriorated when they contact into corrosion agents like moistures and vegetables [5, 6]. As the metal goes into corrosion agents, it oxidized from a zero charge to positively charged ions, and an equivalent amount of electricity must pass from the corrosion agents to the metal so as to neutralize the charge [5, 6]. As a result of this uphill thermodynamic struggle, metal was corroded since it has a strong driving force to return to its native, low energy oxide state as shown in scheme 1.II below [6, 8].



orrosion process of metals

In many industries such as sugar, beverage, tanning, cement and other chemical industries metals are corroded and deteriorated [7, 8]. This is due to electrochemical reaction that occurs on the metal surface when they come in contact with different corrosion agents [7]. This corrosion causes a great loss of economy such as it reduces the thickness, mechanical strength, conductivity, malleability and ductility of metals [8, 9]. It also reduces the cost and efficiency of the machine; it blocks and damages pumps, pipes, boilers and buildings [7, 10]. Corrosion can compromise the safety of operating equipment by causing failure (with catastrophic consequences); for example, pressure vessels, boilers, metallic containers, turbine blades and rotors, bridges, airplane components, and automotive steering mechanisms[8-10].

In light these, chemists, engineers and corrosion specialists have tried several techniques for corrosion preventions like proper selection of shape and size; organic and inorganic coatings, polymeric and nanocoating methods [6, 10]. Several workers (Alam *et al*., 2008, Kalendova *et al*., 2008 and Singh, 2009) used heterocyclic compounds which possessed nitrogen, oxygen and sulphur like primary, secondary, tertiary, quaternary amine, aromatic amine and hetero cyclic aromatic amine as protective of metals from corrosion [5, 7]. They also used rubber and nanocoatings materials like nanocomposite thin film coating and thermal barrier coating on surface of metal as good inhibitive effect against acidic corrosion [7, 9, 10]. But these chemicals release harmful substances which are not suitable for environmental and animals [7, 11]. Therefore, it is necessary to develop methods of selecting inhibitors which are not harmful for environment. To solve this problem, this study is tried to apply natural products like CE for corrosion protection of metal in acidic medium since it was found for environmental eco-friendly and available in affordable price. Therefore, this study is designed to investigate the anticorrosion of CE using weight loss method.

METHODOLOGY AND MATERIALS

Study Area

The present study is conducted in Adigrat University, in northern region of Ethiopia. Adigrat is a city and separate woreda that found in Tigray Region of Ethiopia. It is located in the eastern zone around 900 km far from Addis Ababa which is capital city of Ethiopia with longitude 14°16′N 39°27′E coordinates and latitude 14°16′N 39°27′E with an elevation of 2457 meters above sea level. Adigrat is endowed with cactus plant which is harvested once in a year. The largest pharmaceutical manufacturing plant in Ethiopia, '**Addis Pharmaceuticals Factory SC'**, is also located in Adigrat. It is famous in honey production and cultural food like "*Tihllo*" which is delicious to eat.

Chemical and Reagent

Three cm by three cm iron sheets, distil water, acetone and 1M HCl was used for anticorrosion activity of cactus extract.

Equipment and Instruments

UV spectroscopy use for absorbance measurement during coagulation activity of cactus. Water-bath also used to maintain the temperature instead of thermostat.

2.4 Collection of Samples**:** Mature healthy and fresh leaves of cactus were collected from side of Adigrat town. The collected leaves were washed with fresh water and allowed to dry in oven. Iron metal sheets were purchased from "Mehda Agam" Adigrat market.

Anti-corrosion Activity of cactus by Weight Loss Method

The rectangular form (3 cm x 3 cm) of iron sheets were washed with soap, tap water, distilled water and finally was rinsed with acetone. These samples were dried and stored in desiccators. They were weighted and results were recorded before immersing in1MHCl acid solution. These tested iron sheets were dipped into 20 mL Hydrochloric acid in 100 mL beakers for 5hrs, 24hr and 48hr. After the corrosion test, the samples were removed from the electrolyte, and were washed thoroughly with distilled water, dried and weighed. The weight loss was reported and the inhibition efficiencies was evaluated using the formula [5]: $\text{IE\%} = \frac{W - Wi}{W} \times 100\%$

Where, W is weight loss in absence of inhibitor and WI is weight loss in presence of inhibitor.

The dose effect was evaluated by taking various doses of CE (1mL, 3mL, 6mL and 9mL) and left for 5hrs, 24 hrs and 48hr. To assess the effect of temperature, the iron metal sheets were placed at various temperatures (298k, 308k and 318k) by maintaining in water-bath.

Statistical Analysis

After the data were obtained and recorded, we use data analysis packages such as Microsoft Excel 2007, math type and originlab 8.1. All measurements were done in triplicate and the results were reported as average values ± SD. Besides these, in order to acquire a better understanding for adsorption mode of the inhibitor on the surface of the iron sheets, the data was tested with several adsorption isotherms, including Langmuir, F*rumkin* and T*emkin*. To calculate thermodynamic parameters of the corrosion process, Arrhenius and transition state equations were also used.

RESULT AND DISCUSSION

Anti-Corrosion Activity of CE by Weight Loss Method

In many industries such as sugar, beverage, tanning, cement and other chemical industries, metals are corroded and deteriorated [1-3]. Once these metals are corroded, the mechanical strength is decreased; the conductivity and the applicability also reduce. In order to reduce the impact of corrosion on material and human health, this study used cactus as inhibition agent. The anticorrosion activities of cactus plant are determined by subjecting the iron metal sheets with 1M HCl acid as corrosion agents. The results are presented in table3.1.

Table3.1. The value of Inhibition efficiency, surface coverage area and corrosion rate of cactus CE with HCl at 298k, 308k and 318k.

Cactus extract(mL)	Temperature(k)	K(mmpy)	IE%	θ
0	298	5.2x10^{-3}	-	-
	308	9.99x10^{-3}	-	-
	318	8.47x10^{-3}	-	-
1	298	2.6 x10^{-3}	49.3%	0.5
	308	2.14x10^{-3}	78.5%	0.78
	318	6.75x10^{-3}	20.3%	0.20
3	298	2.3x10^{-3}	55.2%	0.56
	308	2.02x10^{-3}	79.8%	0.79
	318	3.74x10^{-3}	55.9%	0.55
6	298	2.3x10^{-3}	56.6%	0.56
	308	1.91x10^{-3}	80.9%	0.81
	318	2.98x10^{-3}	64.7%	0.65
9	298	1.4x10^{-3}	72.9%	0.73
	308	1.60x10^{-3}	83.9%	0.83
	318	2.10x10^{-3}	75.2%	0.75

The Effect of CE Dose on Anticorrosion Activity of Iron metal Sheets

As shown in Table 3.1, the rate of corrosion is decreased from 7.887x10^{-3} to 1.7x10^{-3} mmpy with increasing dose of inhibitors from 0mL to 9mL. But the inhibition efficiency and surface coverage area are increased from 49% to 77% and 0.49 to 0.77, respectively with increasing inhibitor dose from 1mL to 9mL. This is due the fact that increasing the dose of inhibitors, a larger number of inhibitors molecule are get adsorbed on the metal surface which resulting more coverage of the corroded metal surface [5]. This makes the metal too difficult from further corrosion by the corrosion agents.

Table3.2. the mean value of Inhibition efficiency, surface coverage area and corrosion rate of cactus CE with HCl 298k, 308k and 318k.

Cactus extract(CE)	K(mmpy)	IE%	θ
0mL	7.887x10^{-3}	-	-
1mL	3.82x10^{-3}	49%	0.49
3mL	2.687x10^{-3}	63%	0.63
6mL	2.397x10^{-3}	67%	0.67
9mL	1.7x10^{-3}	77%	0.77

As it can be seen in Fig.3.1, the anticorrosion activity of CE increased with the dose of CE as depicted at three temperature conditions. In all case, the percentage inhibition of CE increased significantly at initial dose of CE. At adding of 1mL CE, the %IE increased from 0.00% to 20.30% at 318k, 0.00%to 49.30% at 298k, and 0.00% to 78.50% at 308k. But %IE of CE increased constantly as the dose of CE is further increased. This constant increment of inhibition efficiency with cactus dose might be due to the fact that the competition of adsorbate on iron metal surface increased. This indicates the iron metal surface is in the way of completely covering by inhibitors.

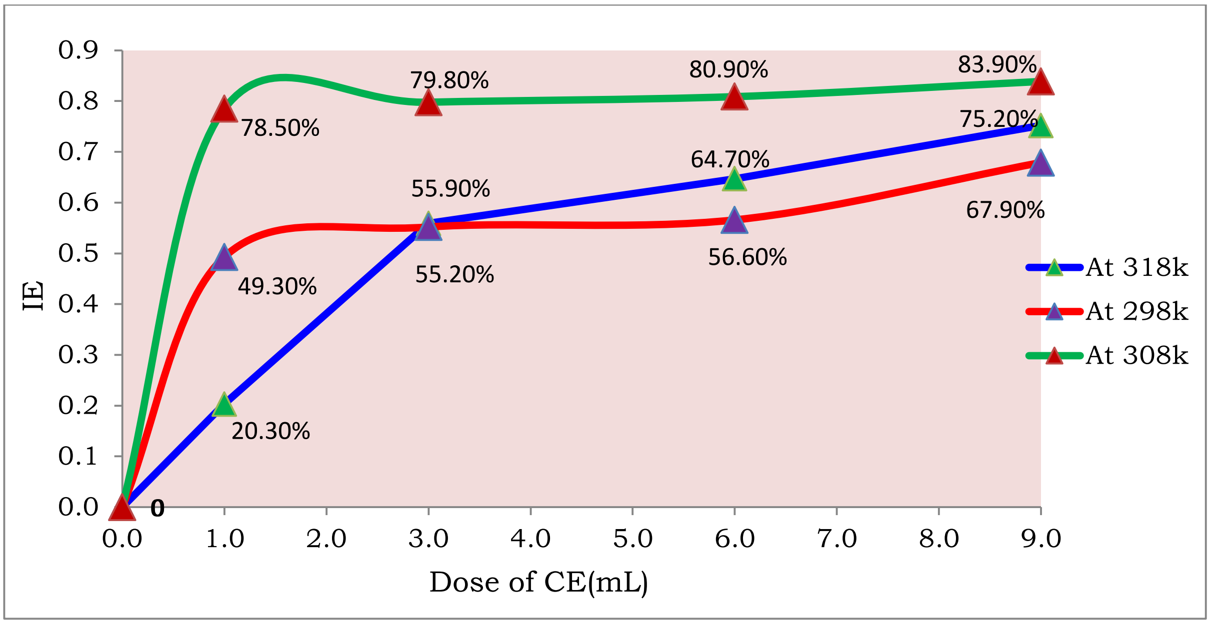


Fig.3.1. the anticorrosion potential of CE at different dosages

Effect of Contact Time on Anticorrosion Activity of CE

The effect of contact time on anticorrosion activity of CE on iron metal sheets can be evaluated by leaving the metal sheets in different time period (5hr, 24hr and 48hr). As shown in Fig.3.2, the percentage inhibition efficiency of CE increased as the contact time increased in a certain limit. This reason why when the solution allow a long time in the tested solution, there is formation of stable complex between adsorbate and adsobent. The adsorbate gets the chance to spend their time on adsorbent surfaces and cover the uninhibited iron metal surface completely.

This increment of inhibition efficiency of CE with immersed time reflects the strong adsorption interaction between the constituents present in the CE on the surface of iron metal sheets; resulting in a more protective layer formed at iron metal sheets. Thus, the anticorrosion activity of CE increased with the contact time.

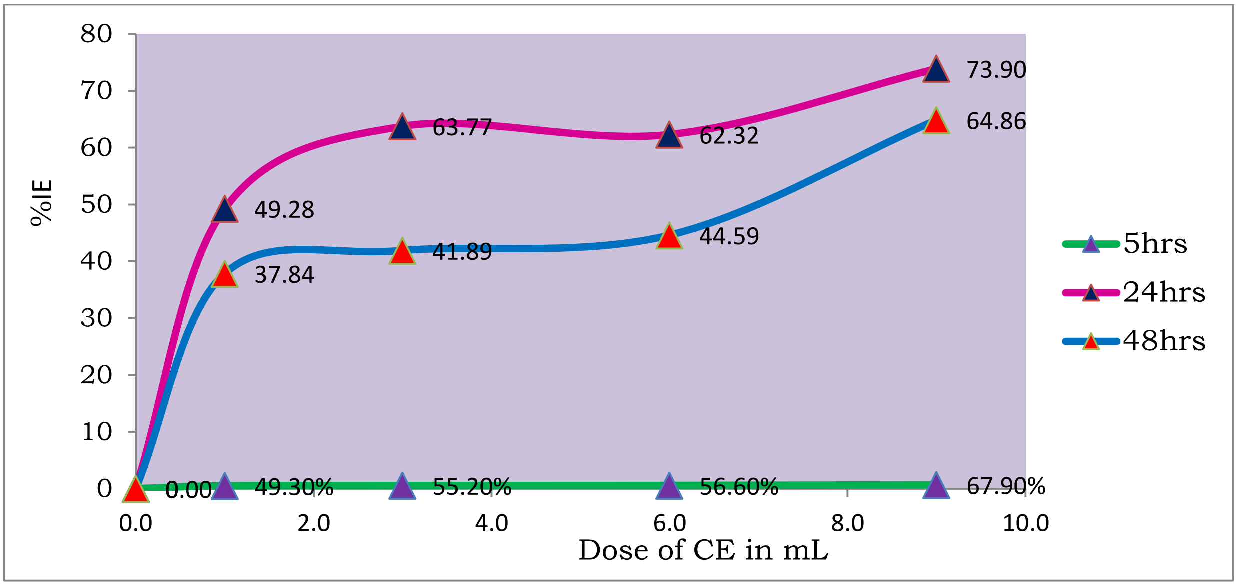


Fig.3.2. Effect of contact time on anticorrosion activity of CE

Effect of Temperature on Anticorrosion Activity of CE

As shown fig.3.3, the %IE of CE is increased as the temperature increased from 298k to 308k, but the %IE show a decrement as the temperature increased from 308k to 318k. This decrement in %IE of CE at higher temperature might be at an elevated temperature, desorption of pre-adsorbed inhibitor molecules occur from metal surface; decomposition and rearrangement of some inhibitors may take place; heterogeneous reaction rate increases at uninhibited metal surface and corrosion rate linearly increases with the increase of temperature [4, 8]. This observation is attributable to dissolution process of iron metal sheets and partial desorption of the inhibitor from the metal surface occur at higher temperature.

At higher temperature desorption of pre-adsorbed inhibitor molecules occur from metal surface, and at lower temperature the activation energy required to initiate interaction between iron metal and CE. Therefore, the anticorrosion activity of CE affected by temperature; the inhibition efficiency is lower at lower and at higher temperature.

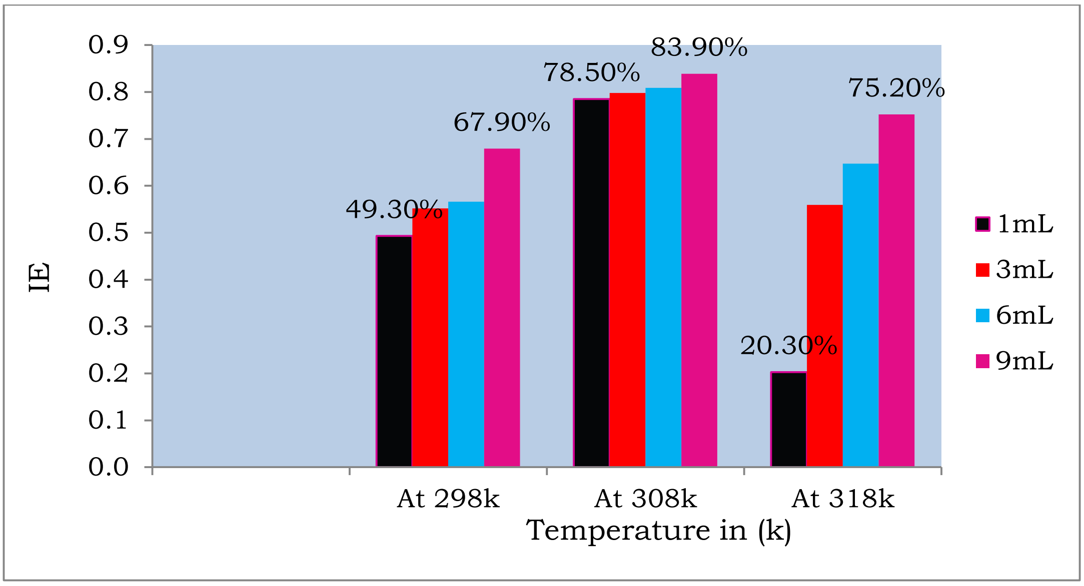


Fig.3.3. Effect of temperature on anticorrosion activity of CE

Adsorption Models

The parameters like surface coverage (θ) and %IE values for different dose of the inhibitors in1M HCl medium was evaluated by weight loss method. The data that obtained from weight loss method were tested graphically to find suitable adsorption mode to describe the adsorption characteristics of CE. In order to acquire a better clue for adsorption mode of the inhibitor on the surface of the iron sheets, the data was checked with several adsorption isotherms, including Langmuir, F*rumkin* and T*emkin [8, 9]*.

Langmuir Adsorption

A plot of Log (Ө/C) against Log C (Fig3.4) shows a straight line indicating that adsorption follows the Langmuir adsorption model which is linear (Table3.3).

Table3.3. Values of Langmuir parameters

Temperature	Equation	slope	R^2
298k	Y=0.888X + 0.306	0.888	0.995
308k	Y=0.973X + 0.11	0.973	0.999
318k	Y=0.728X + 0.395	0.728	0.999

R^2= coefficient of determination

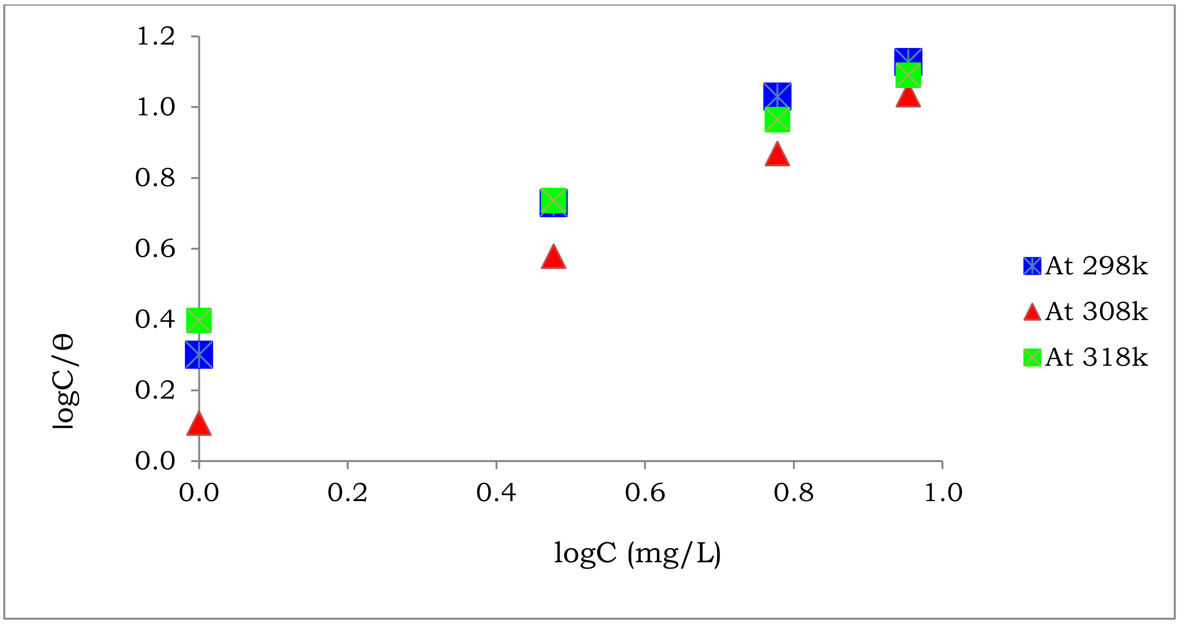


Fig.3.4. Lumgumuir adsorption isotherms for CE at different temperature

Temkin Adsorption Isotherm

A straight line was obtained when the surface coverage (Θ) was plotted against log C for the inhibitor at different temperature by maintaining in water-bath [8]. The linear line of CE at various temperatures (298k, 308k and 318k) shows that the adsorption follows a Temkin adsorption isotherm (Fig.3. 5).

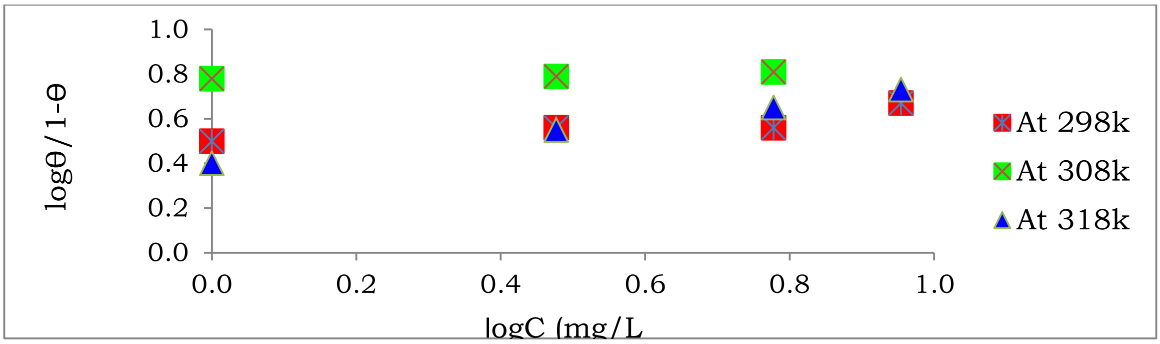


Fig.3.5.II. Temkin adsorption isotherms for CE at different temperature

Table3.4. Values of Temkin parameters

Temperature	equation	slope	R^2
298k	Y=0.147X + 0.490	0.147	0.758
308k	Y=0.049X + 0.774	0.049	0.885
318k	Y=0.339X + 0.394	0.339	0.991

Frumkin Adsorption Isotherm

The plot of %IE against Log C (Fig.3.6.) shows a linear line which makes noticeable the adsorption of the inhibitor on iron metal sheets match with the Frumkin isotherm (Saratha *et al*., 2009 and Patrick *et al*., 2006).

As shown Fig3.6. and Table3.5, the regression value departure from unity. This may due to the fact that molecular groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction [8, 9].

Table3.5. Values of Frumkin parameters

Temperature	equation	slope	R^2
298k	Y=0.165X + 0.480	0.165	0.794
308k	Y=0.05X + 0.780	0.05	0.821
318k	Y=0.337X + 0.396	0.337	0.992

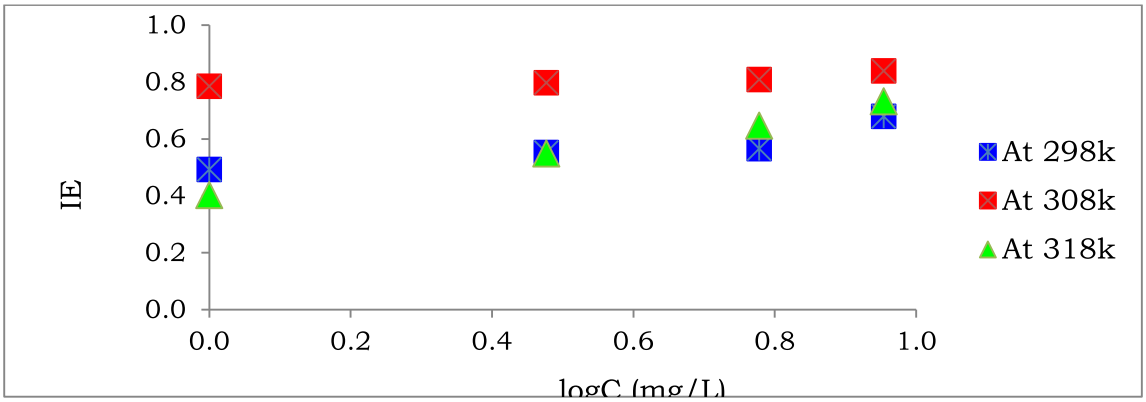


Fig.3.6. Frumkin adsorption isotherms for CE at different temperature

The straight line that obtained from Frumkin adsorption isotherms, Temkin adsorption isotherms and Lumgumuir adsorption isotherms indicates the adsorption of asorbate on adsorbent is monolayer and highly interdependent with each other.

Thermodynamic Studies

Thermodynamic parameters; free energy (ΔG), activation energy (Ea) and Heat of adsorption Qads of *CE* on iron metal surface were calculated using different Equations [8-9]. The Value of heat of adsorption of *CE* on iron metal surface was calculated using equation given below [8-10]:

$$Q_{ads} = 2.305R\left[\log\left\{\frac{\theta_2}{1-\theta_2}\right\} - \log\left\{\frac{\theta_1}{1-\theta_1}\right\}\right]x\left\{\frac{T_1T_2}{T_2-T_1}\right\}KJ/mol$$

Where Qads is the heat of adsorption, R is the universal gas constant, Θ_1 and Θ_2 are the degrees of surface coverage of the inhibitors at temperatures T_1 and T_2, respectively.

The activation energy for the corrosion of iron metal sheets in 1M HCl solution was evaluated using the Arrhenius equation given below [8, 10]:

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

Where, Ea is the activation energy of the reaction, R is the gas constant, T is the temperature and, considering a change in temperature from 303 K (T_1) to 313 K (T_2), the corresponding values of the corrosion rates at these temperatures are CR_1 and CR_2, respectively.

Table3.6. Value of thermodynamic parameters

Temperature range in "k"	Dose of CE	Ea kJ/mol	Qads kJ/mol
308 to 318	9mL	93.40	-25979.95
308 to 318	6mL	50.09	-11013.389
308 to 318	3mL	29.21	-8140.22
308 to 318	1mL	22.11	-4770.91

As shown in Table3.6, the Value of heat of adsorption of *CE* on iron metal sheets between 318k and 318 K are-25979.95 kJ/mol, -11013.389 kJ/mol, -8140.22 kJ/mol, and-4770.91 kJ/mol at 9mL, 6mL, 3mL and 1mL CE dose, respectively. The large negative value of heat of adsorption indicates the stable interaction of CE on iron metal sheets. Besides, the negative values of heat of adsorption also indicate that adsorption of CE on iron metal sheets is spontaneous and occurs via physical Adsorption mechanism.

The Value of activation energy of *CE* on iron metal sheets of between 318k and 318 K is 93.40kJ/mol, 50.09kJ/mol, and 29.21kJ/mol, and 22.11kJ/mol at 9mL, 6mL, 3mL and 1mL CE dose, respectively. The large value of activation energy implies that the more stable interactions between the adsorbate and adsorbent during anticorrosion activity of CE. This is due to the fact that Activation energy is the energy that required oxidizing metal; it implies that more energy needed to the system for the corrosion to take place. Therefore, the inhibition efficiency of CE increased with dose.

The value of free energy also can be calculated at different temperature using the equation:

$\Delta G = -2.303RT[\log C - \log \frac{\theta}{1-\theta} + 1.72]$ [4, 8] and the results were presented in table3.7.

Table3.7. Value of free energy at 298K, 308K and 318K

Temperature (K)	ΔG
318	-6795.44
308	-13362.44
298	-9797.53

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The negative value of free energy results shows that the interaction between inhibitor and adsorbent is an exothermic process (Table3.7).

CONCLUSION

The anticorrosion activity of CE was investigated using weight loss method. The experimental results showed that upon increasing of inhibitor doses the corrosion rate is reduced. The inhibition efficiencies and surface coverage area of CE increases as function of its concentration and immersed time.

The straight line of Lumgumuir, Temkin and Frumkin adsorption isotherms indicate the adsorption of CE on iron metal sheets is mono-adsorption. The negative value of heat of adsorption also reveals the adsorption process is exothermic. This is the reason why the inhibition efficiency of CE decreased as the temperature increased. The larger positive value of activation energy and the large negative value of ΔG and ΔHad indicate the thermodynamic stability of CE.

The anticorrosion activities of CE have ample significance in this world since it is available at low price, highly efficient and eco-friendly. The inhibitor produces thin surface film on interface of metal surface. The inhibitor has good Inhibition efficiency and Surface Coverage area and minimizes the attack of corrosive substance.

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