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Corrosion Inhibition at Mild Steel Surface in Acidic Media by Ziziphus Jujuba Plant

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ABSTRACT

The effect of Ziziphus jujuba extract on the corrosion inhibition of mild steel in acidic solution was studied using chemical and electrochemical techniques. It was found from the results of weight loss method that the inhibition efficiency increased with increase in the plant extract up to 15 ppm. It indicates that 15 ppm is the optimum concentration to get maximum corrosion protection for mild steel in acidic medium. The results obtained from the chemical and electrochemical measurements are in good agreement. Organic moieties present in the extract are found responsible for effective performance of inhibitor which was well supported by FTIR studies. The potentio dynamic polarization studies revealed that the plant extract acts as mixed type inhibitors. The surface characteristics of the inhibited and uninhibited mild steel were investigated by Scanning Electron Microscopic studies.

KEYWORDS: *Ziziphus jujuba, acidic, mild, steel, corrosion, inhibition, plant, extract, media, techniques.*

Introduction

Corrosion is a natural process that converts a refined metal into a more chemically stable oxide. It is the gradual destruction of materials (usually a metal) by chemical or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.

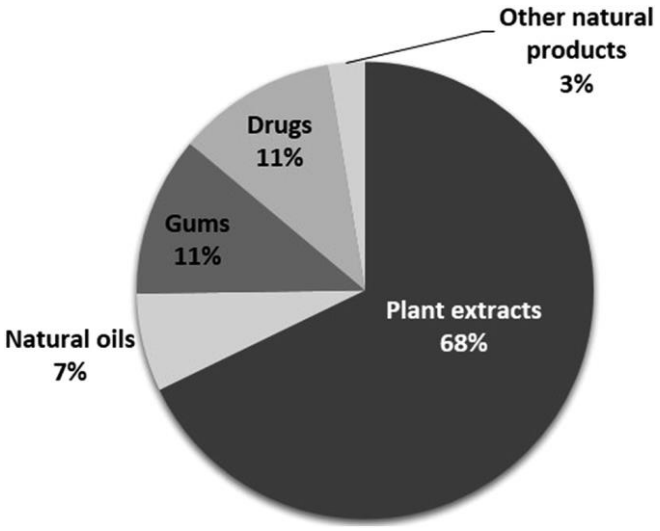

Fig.1.Corrosion inhibitor by natural plant extracts is of higher percentage

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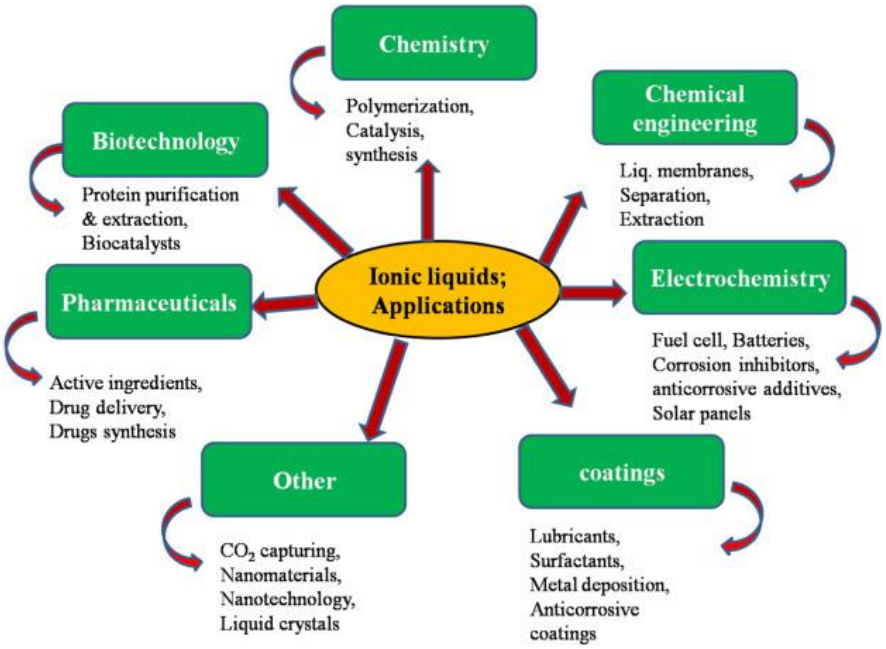
In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen, hydrogen or hydroxide. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion.

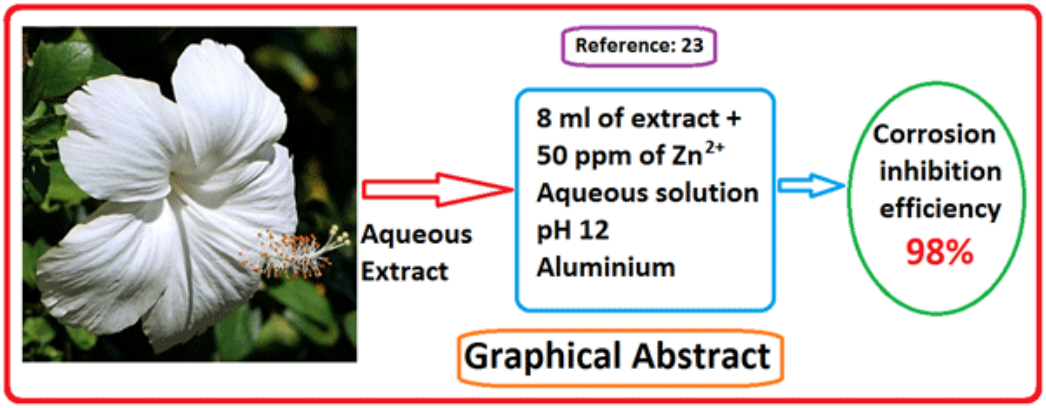


This type of damage typically produces oxide(s) or salt(s) of the original metal and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

A corrosion inhibitor or anti-corrosive is a chemical compound that, when added to a liquid or gas, decreases the corrosion rate of a material, typically a metal or an alloy, that comes into contact with the fluid. The effectiveness of a corrosion inhibitor depends on fluid composition, quantity of water, and flow regime. Corrosion inhibitors are common in industry, and also found in over-the-counter products, typically in spray form in combination with a lubricant and sometimes a penetrating oil. They may be added to water to prevent leaching of lead or copper from pipes. [1,2]

A common mechanism for inhibiting corrosion involves formation of a coating, often a passivation layer, which prevents access of the corrosive substance to the metal. Permanent treatments such as chrome plating are not generally considered inhibitors, however: corrosion inhibitors are additives to the fluids that surround the metal or related object.

Various examples of plant extracts as corrosion inhibitors (ecofriendly approach)



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Natural extracts have been widely used to protect metal materials from corrosion. The efficiency of these extracts as corrosion inhibitors is commonly evaluated through electrochemical tests, which include techniques such as potentiodynamic polarization, electrochemical impedance spectroscopy, and weight loss measurement. The inhibition efficiency of different extract concentrations is a valuable indicator to obtain a clear outlook to choose an extract for a particular purpose. A complementary vision of the effectiveness of green extracts to inhibit the corrosion of metals is obtained by means of surface characterizations; atomic force microscopy, scanning electron microscopy, and X-ray photoelectron spectroscopy analysis are experimental techniques widely used for this purpose. Moreover, theoretical studies are usually addressed to elucidate the nature of the corrosion inhibitor—metal surface interactions. In addition, calculations have been employed to predict how other organic substances behave on metal surfaces and to provide experimental work with fresh proposals. Additional studies regarding plant extracts as corrosion inhibitors on metals are needed to produce solutions for industrial purposes.

Various metal corrosions have been inhibited in acidic or alkaline media

The inhibition performance of extracts of *Ziziphus* spp. on mild steel corrosion in 0.5 M H_2SO_4 and 0.5 M HCl was investigated using gravimetric, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies. The gravimetric results indicate that *Ziziphus* spp.leaves extract exhibits good inhibition efficiency in both the acids. Furthermore, the inhibition efficiency decreases with increase in temperature. Polarization measurements showed that the studied inhibitor is mixed type in both acids with significant reduction of cathodic and anodic current densities. Electrochemical impedance spectroscopy measurements revealed that the charge transfer resistance increases with increase in the concentration of *Ziziphus* spp. extracts. Various thermodynamic parameters such as activation energy, activation enthalpy and activation entropy are evaluated and discussed. [3,4] Adsorption thermodynamic parameters are also computed, and SEM was used to analyze the surface adsorbed film.

Table.1. Green approach to corrosion inhibition of Aluminium and Copper by *Ziziphus* spp.

Immersion Period (h)	Aluminium		Copper	
	Correlation coefficient (R^2)	(adsorption coefficient)	Correlation coefficient (R^2)	(adsorption coefficient)
6	0.904	0.9515	0.965	2.1141
12	0.810	1.0482	0.972	3.4246
18	0.849	1.1547	0.980	4.4643
24	0.858	1.3441	0.982	5.0761
48	0.997	3.1645	0.995	10.869
72	0.996	4.2194	0.999	11.764

Discussion

Many plant extracts utilized in corrosion inhibition example *Jatropha curcas*

Inhibition of corrosion of mild steel in sulphuric acid by acidic extract of *Jatropha curcas* leaves has been studied using weight loss and thermometric measurements. It was found that the leaves extract act as a good corrosion inhibitor for mild steel in all concentrations of the extract. The inhibition action depends on the concentration of the *Jatropha curcas* leaves extract in the acid solution. Results for weight loss and thermometric measurements indicate that inhibition efficiency increase with increasing inhibitor concentration. The adsorption of *Jatropha curcas* leaves extract on the surface of the mild steel specimens obeys Langmuir adsorption isotherm. Based on the results, *Jatropha curcas* leaves extract is recommended for use in industries as a replacement for toxic chemical inhibitors[5,6]

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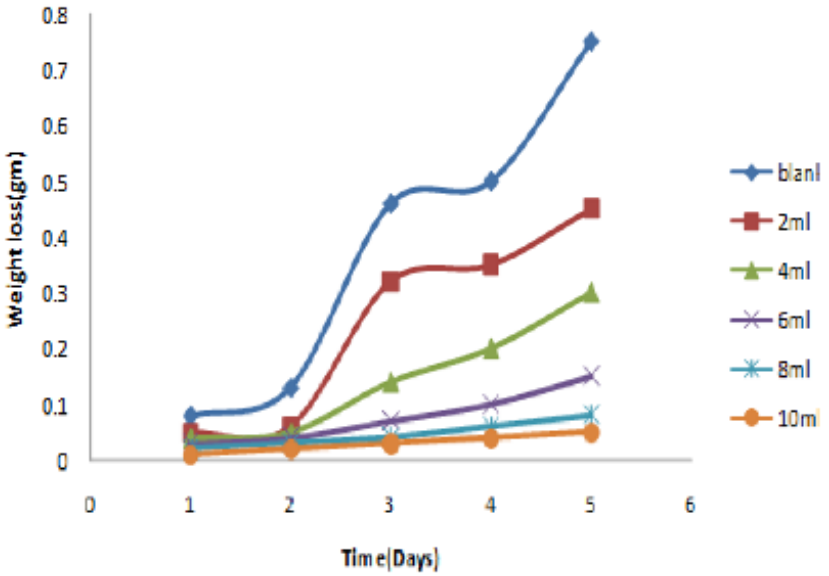

Fig.2 .Variation of weight loss with time for the corrosion of mild steel in H 2 SO 4 solution containing various another53ation of *Jatropha curcas* leaves extract.

Utilization of other metals (like aluminium) in inhibition mechanism by *Ziziphus jujuba*

Another example is inhibition of corrosion of aluminium in 1N NaOH by leaves extract of *Ziziphus jujuba* was studied using chemical and electrochemical techniques. It was found that the leaves of inhibits the base induced corrosion of aluminium.The inhibition efficiency increased with increase in concentration of *Ziziphus jujuba* extract and reached the maximum of 76.4%,that decreases with rise in temperature.The inhibition action of *Ziziphus jujuba* is discussed in view of Langmuir adsorption isotherm.It has been observed that the adsorption of the extract on aluminium surface is a spontaneous process. Polarization measurements showed that *Ziziphus jujuba* extract acts as mixed type inhibitor. The surface morphology of aluminium in the absence and presence of *Ziziphus jujuba* extract in 1N NaOH solution, was studied using scanning electron microscopy. Results obtained from chemical and electrochemical techniques were in good agreement.Thermodynamic parameters such as activation energy and free energy of adsorption were also calculated to explain the inhibition mechanism. The plant extract provides a good protection to aluminium corrosion.

Fig.3. *Ziziphus jujuba* plant

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Utilization of other metals (carbon steel) in inhibition mechanism by *Ziziphus jujuba*

The inhibitive action of the *Ziziphus jujuba* leaves extract against corrosion of carbon steel in 1N HCl was investigated using weight loss measurements, gasometric method, potentiodynamic polarization curves and electrochemical impedance spectroscopy methods. The results obtained from these methods indicate that the extracts perform as a good green corrosion inhibitor in acidic medium and inhibition efficiency increased with extracts concentration. The maximum inhibition efficiency of 82.2% was obtained at the best concentration of 800 ppm of *Ziziphus jujuba* extract. The effects of temperature and immersion time on carbon steel in 1N HCl were also studied. Polarization curves show that *Ziziphus jujuba* extract act as a mixed-type inhibitor in hydrochloric acid. EIS shows that the capacitance of double layer decreases and charge-transfer resistance increase with the optimum concentration of 800 ppm of ZJL extract, confirming the adsorption process mechanism. The adsorption of *Ziziphus jujuba* extract on the surface of the carbon steel follows the Langmuir adsorption isotherm. The mechanism of inhibition was confirmed by kinetic and thermodynamic parameters obtained from 303K to 363K temperatures using weight loss method. The metallurgical microscope results established the formation of a protective layer on the carbon steel surface.[7,8]

Several plant extracts are used as metal corrosion inhibitors

Recently, several natural plants such as, *Combretum bracteosum,Medicago Sativa, Justicia gendarussa, Jasminum nudiflorum, Vitex negundo, Prosopis cineraria, Emblica officinalis, Solanam Xanthocarpum, Kopsia singapurensis, Heinsia crinata, Dacryodis edulis, Murraya koenigii, Oxandra asbeckii, Sennaauriculata* have been used as corrosion inhibitors commonly known as green corrosion inhibitors. This is considered to be an ecofriendly approach.

***Ziziphus jujuba* shrub**

Ziziphus jujuba is a shrub belongs to family Rhamnaceae and it is known as “Elantai” in Tamil. It is distributed in many parts of the world but mainly populates in tropic and warm, temperate region. Phytochemically, it has high medicinal value due to the presence of cyclopeptide alkaloids, polysaccharides, flavonoids, terpenoids, tannins, saponins, pectin, triterpenoic acids and lipids . It has a major part in treatment of various ailments like analgesic, antipyretic, anti-inflammatory, sedative, antioxidant, antibacterial, GIT protective, antispasmodic, antidiabetic and antifungal activities [23].The present research work is devoted to study the inhibition characteristics of *Ziziphus jujuba* leaves extract on the corrosion of carbon steel in 1N HCl medium, using weight loss, gasometric, Tafel polarization and AC impedance studies. From this, a suitable mechanism regarding the mode of inhibition was proposed. Surface morphology on the carbon steel with and without inhibitor was made to confirm the adsorptive layer on the surface of carbon steel.

Results of the Present investigation

Utilization of *Ziziphus jujuba* roots extract inhibiting mild steel corrosion in 1M HCl

The inhibition of mild steel in 1 M HCl solution with aqueous extract of *Ziziphus jujuba* roots was studied by weight loss method at 303-333K temperatures. It was found that inhibition efficiency increased with increase in concentration of extract and decreased with increase in temperature. Maximum 62.68% inhibition efficiency was observed at 303 K and at 8% (v/v) concentration of extract. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Physiorption is proposed by the values of Gibbs free energy, variation in inhibition energy with temperature and with activation energy values trend. Negative values of Gibbs energy reveals the spontaneity of inhibition process in extract at studied temperatures (as reviewed from prior investigation carried out)

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Temperature (K)	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol/K)
303 K	-7.84794	-35.08	-89.8748
313 K	-7.05217		-89.5458
323 K	-5.7499		-90.8053
333 K	-5.28394		-89.4777

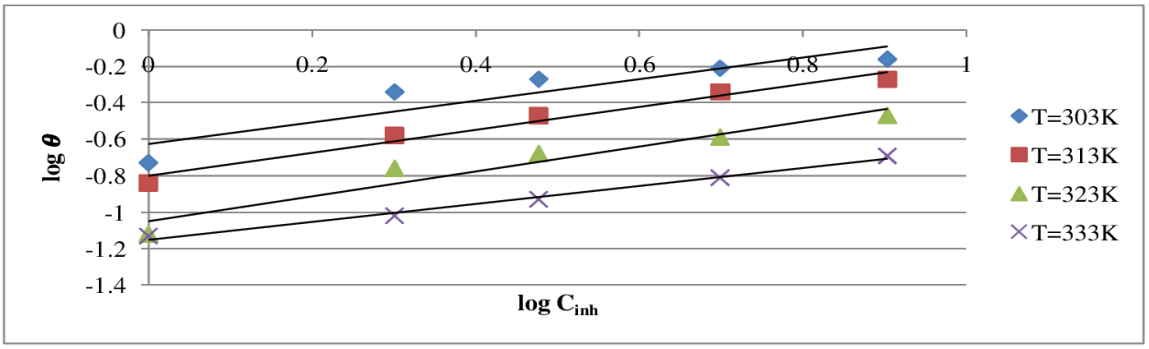
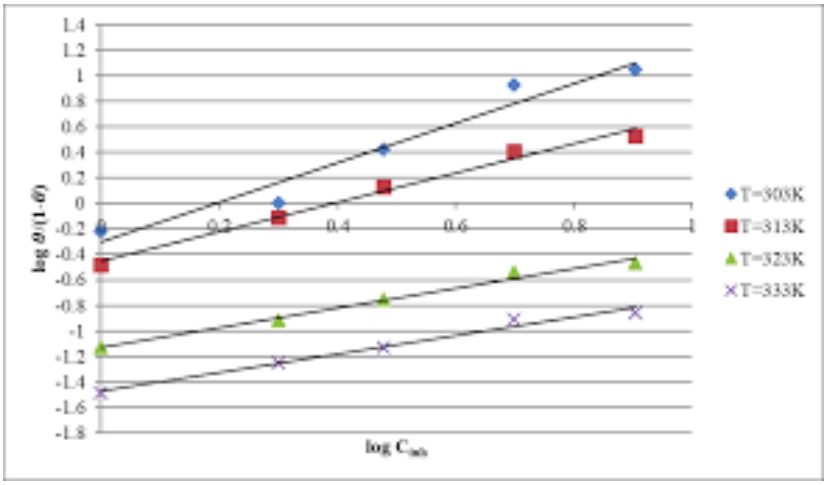


Fig.4. Utilization of *Ziziphus jujuba* root extract inhibiting mild steel corrosion in 1M HCl

Weight loss method was used to assess the inhibition of mild steel corrosion in 1M HCl solution with aqueous extract of *Ziziphus jujuba* leaves at 303 to 333K temperatures. It was found that *Ziziphus jujuba* leaves extract retarded the dissolution of mild steel in 1M HCl solution. The inhibition efficiency increases with a rise in the concentration of extract and decreased with increase in temperature. Maximum 88.54% inhibition efficiency was observed at 303 K and 8% (v/v) composition of the extract. Adsorption of extract at mild steel surface follows Langmuir adsorption isotherm. Values of Gibbs free energy, variation in inhibition energy with temperature and with activation energy values trend proposed the physisorption. Negative values of Gibbs energy propose the spontaneous process of inhibition process in the extract at studied temperatures.[9,10]



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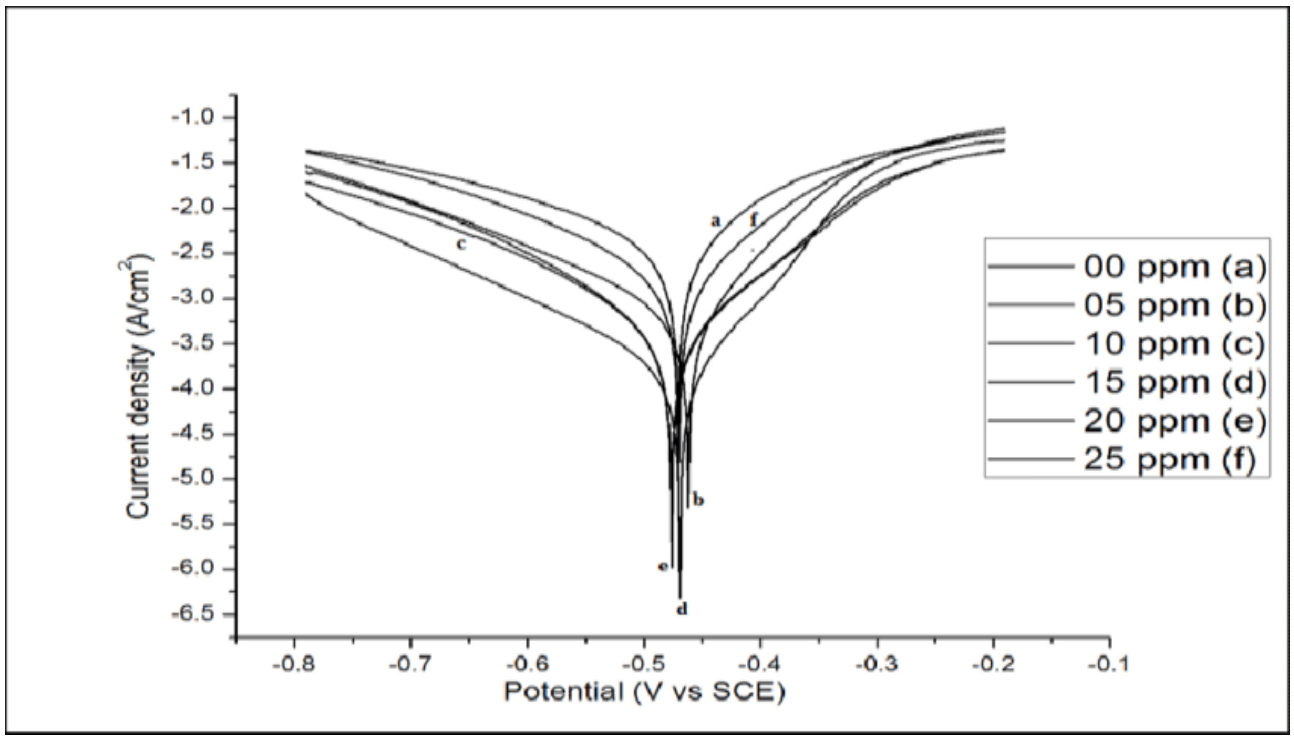

Fig.5. FT-IR spectrum of *Ziziphus jujuba* leaves extract inhibiting mild steel corrosion in 1M HCl

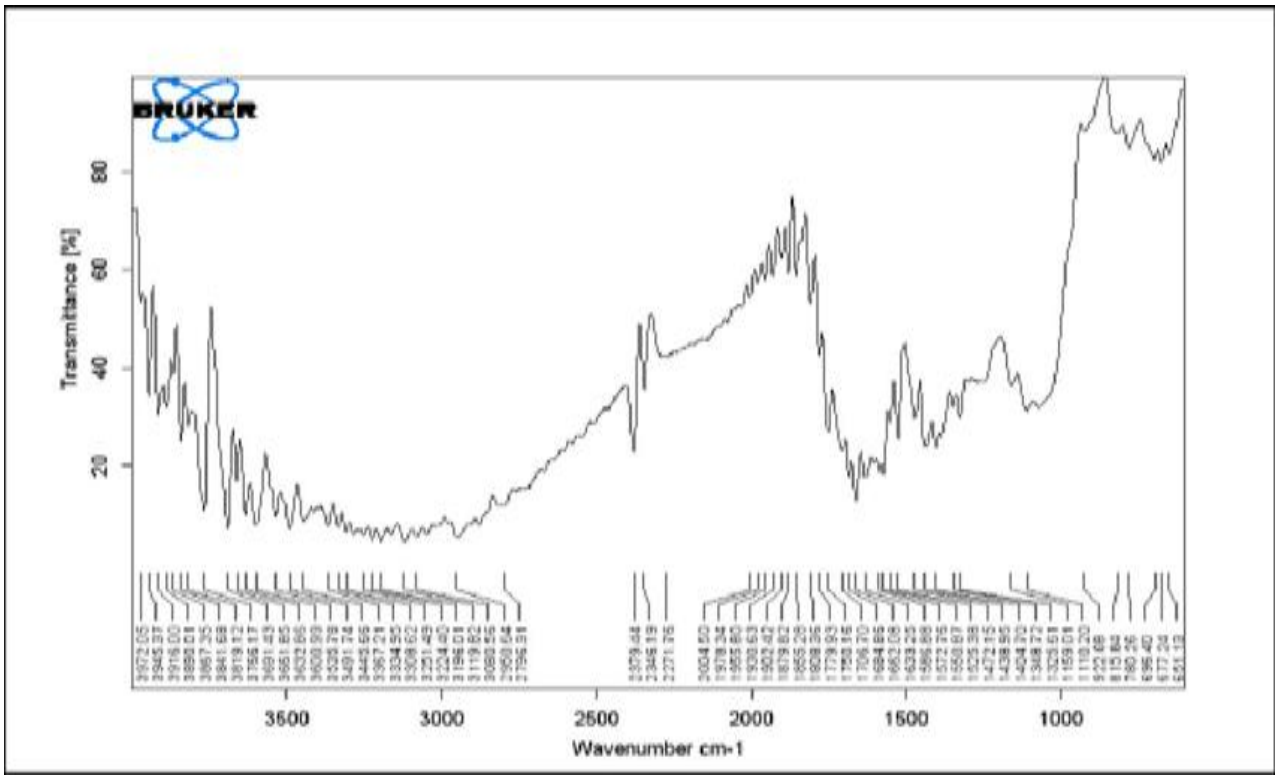

Fig. 6. Utilization of *Ziziphus jujuba* stem extract inhibiting mild steel corrosion in 1M HCl

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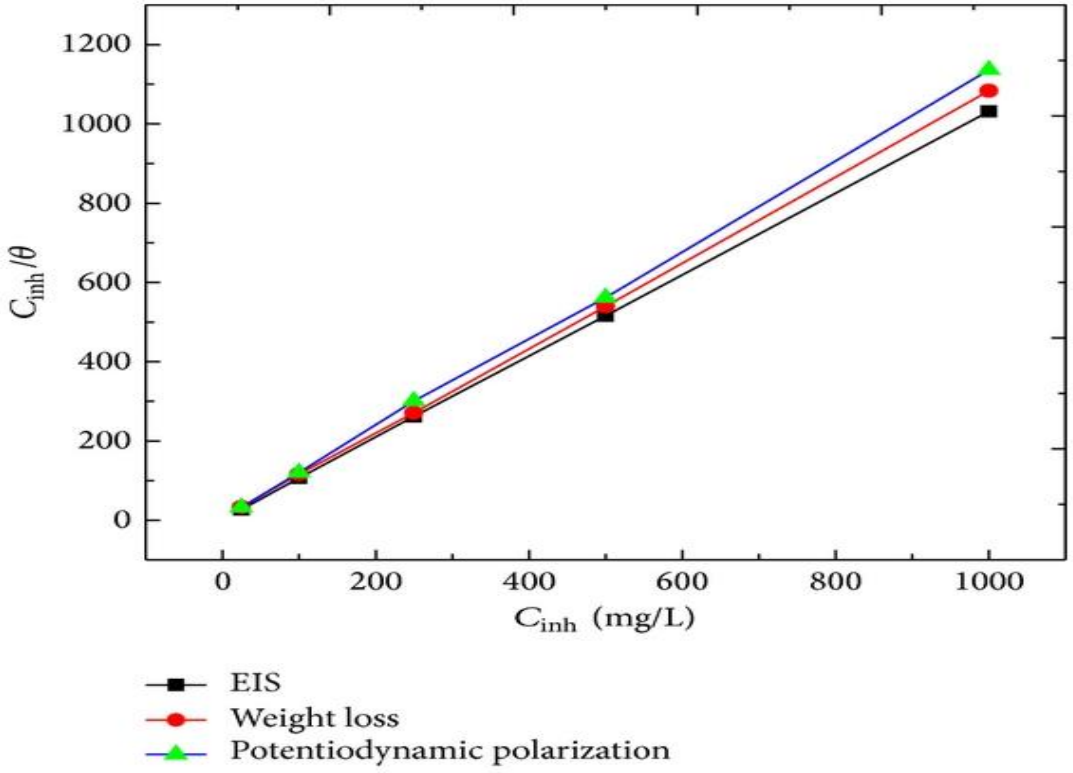
C_{inh} in (v/v)%	I E (%)			
	30°C	40°C	50°C	60°C
1	28.04	14.18	11.37	4.68
2	48.78	26.95	22.27	10.43
3	54.88	35.46	30.33	14.75
5	67.07	44.68	37.91	20.50
8	78.05	53.19	42.18	22.66



Conclusions

The aqueous extract of *Ziziphus jujuba* plant parts and its varied molecular weight fraction acts as a great corrosion inhibitor of mild steel in an acidic medium of HCl. The results achieved by gravimetric, weight loss method, electrochemical-impedance spectroscopy and anodic and cathodic polarization curves corroborate with each other. The mechanism of inhibition occurs through adsorption on the metal surface, preventing both iron dissolution and hydrogen evolution, being, therefore, a mixed inhibitor, as shown by the potentiodynamic polarization curves. Electrochemical results showed that the addition of the extracts did not change the anodic and cathodic mechanism.

Ziziphus jujuba extracts acted as an effective corrosion inhibitor for mild steel in 1 M HCl solution. The polarization studies showed that *Ziziphus jujuba* extract was a good inhibitor and its corrosion efficiency increased with the inhibitor concentration. From the EIS plots of mild steel, it is clear that the charge transfer resistance increased with increase in *Ziziphus jujuba* extract. Inhibition efficiency

obtained from weight loss measurements was in good agreement with polarization and EIS methods. The adsorption of the *Ziziphus jujuba* extracts of mild steel in 1 M HCl solution obeys the Langmuir adsorption isotherm and the SEM studies showed the formation of inhibitor film on mild steel surface.[11]

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