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Anti-Corrosive nature of *Kair (Capparis decidua)* shrubs extract against zinc metal in acidic environments

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Abstract

The corrosion of metals and their alloys has prompted an increase in research efforts to lessen the harm caused by the corrosion process. The study analyses the ability of Kair (*Capparis decidua*) shrub extract to suppress corrosion on metal in 0.1 N HCl and 0.1 N H_2SO_4 solutions using thermometric and weight loss techniques. At all extract concentrations, it was shown that the shrub extract efficiently prevents zinc corrosion. The inhibitory action is determined by the concentration of the shrub extract in the acidic solution. The findings of mass loss measurements indicate that inhibition efficiency increases with inhibitor concentration. Based on thermodynamic considerations, the extract's adsorption is exothermic and spontaneous. From the results and findings of the study, a physical adsorption mechanism is proposed for the adsorption of ethanol extract of Kair shrubs extract on zinc surface.

The inhibitory efficiency was projected using certain methods at 303K, 313K, and 323K temperatures. As the extract's concentration rose, the inhibition effectiveness rose as well, demonstrating the shrub extract's inhibitory ability. The extrapolation of enthalpy, entropy change, activation energy, and Gibbs free energy provided evidence for this. The thermodynamic variable demonstrates that physisorption was the mechanism of inhibition. Therefore, the current research shows a new, ecologically safe, and effective corrosion inhibitor for protecting zinc surfaces in acidic environments.

Keyword: Kair shrubs, corrosion inhibition, mass loss measurements, Langmuir adsorption.

Introduction

The International Organisation for Standardisation (ISO) and the International Union of Pure and Applied Chemistry (IUPAC) define corrosion as "the physical interaction of a metal with its environment that results in changes to the metal's properties and may cause the metal, its environment, or the technical system of which they are a part to significantly lose some of their functionalities." Blockages in pipes triggered by solid corrosion products increase the complexity and cost of equipment that must be constructed to withstand a certain amount of corrosion and allow corroded components to be conveniently replaced, decreased value of goods as a result of deteriorating appearance, fluid contamination in vessels and pipes, mechanical damage to valves, pumps, etc., risks or injuries to people resulting from structural failure or breakdown (Edraki *et al*., 2022; Pourhashem *et al*., 2020).

The heterocyclic ring structures of synthetic organic molecules are extremely comparable to the phytochemicals found in abundant supply in plants. Corrosion can be significantly inhibited by the presence of tannins, pectin, alkaloids, amino acids, fatty acids, etc. Plant, seed, flower, fruit, and leaf extracts displayed superior anticorrosive qualities. The use of plant products as corrosion inhibitors are justified by the phytochemical compounds present therein, with molecular and electronic structures bearing close similarity to those of conventional organic inhibitor molecules (Baskar *et al*., 2023). The drawbacks of employing plant extracts as environmentally friendly corrosion inhibitors include time-consuming extraction processes, product contaminants, and the seldom identification of the active ingredient responsible for corrosion inhibition (Ghiasvandnia *et al*., 2023).

Capparis decidua (Forsk.) is belonging to family Capparidaceae, yet important medicinal plant. The plant is reported to contain Phytochemicals including alkaloids, terpenoids, glycosides and some fatty acids. The plant have significant pharmacological activities like hypercholesterolemic, anti-inflammatory and analgesic, antidiabeti, antimicrobial, antiplaque, antihypertensive, antihelmintic & purgativ activities.

Al-Bataineh *et al.,* (2022) obtained data by mass-loss and polarization experiments confirm the likely usefulness of *C. decidua* crude as a green inhibitor of aluminium corrosion in acidic medium. The energy of activation, E_a, of aluminium dissolution in acidic solution without the inhibitor was found to be higher than that with inhibitor. The extract of *Capparis decidua* seeds has been observed by Pratihar *et al.* (2015) to be an efficient inhibitor of copper in acidic medium, with a considerably high inhibitory efficacy of 94.60% at its concentration of 1.0426 g/L for 72-hour immersion duration. The phytochemical components found in *C. decidua* seeds account for their high inhibitory effectiveness. The presence of numerous bonds and heteroatoms, such as oxygen and nitrogen, in these phytochemical ingredients increases the inhibitor's adsorptive tendency.

The suitability of plant extracts for industrial usage has not been well studied or documented. This research aims to investigate if using plant Kair *(Capparis decidua)* shrubs in acidic media may lessen zinc corrosion. Additionally, field testing was done to determine the industrial application of the plant extract in electrochemical enterprises that employ the pickling technique for surface treatment.

Materials

Extraction of plants Shrubs

This study investigated the potential corrosion-inhibitory effects of an extract from Kair (*Capparis decidua*) shrubs using mass loss and electrochemical methods. The seeds were collected in Rajasthan's Nagaur region. After being crushed into a powder and dried outdoors, the gathered shrubs were immersed in 95% ethanol for three days. The extract was then made using the Soxhlet method.

Mass Loss Method

Mass loss is the most widely used method for assessing damage caused by corrosion. You can determine how much metal an object would lose due to corrosion by weighing it both before and after exposure (Fouda *et al*., 2018).

Using the following formula, the inhibitor's efficacy in preventing inhibition was determined:

$$\mathbf{IE\%} = \frac{w_0 - w_i}{w_0} \times \mathbf{100}$$

IE- Inhibition efficiency; W is the weight loss with (i) or without (0) influence of the inhibitor.

Surface coverage (θ) was calculated using the following formula

$$\text{Surface Coverage }(\theta) = \frac{\Delta M_u - \Delta M_i}{\Delta M_u}$$

Langmuir Adsorption Isotherm

Several adsorption isotherms, including as Langmuir, Frumkin, Temkin, and Freundlich, were used to characterise the adsorption of shrub extracts on the zinc surface in HCl and H_2SO_4 solution. The Langmuir adsorption isotherm best described the experimental data, which can be expressed as

$$\mathbf{C/\theta = (1/Kads) + C}$$

Where C is a concentration of inhibitor molecules, θ is surface coverage, and Kads is the equilibrium constant of the adsorption process.

Determination of Thermodynamic parameters:

Various thermodynamic parameters such as free energy of adsorption (ΔG^0_{ads}), and enthalpy of adsorption (ΔH^0_{ads}) were calculated from the results of temperature study.

Results and Discussion

Following immersion in 0.1 N HCl and H2SO4 solution in open air at 303+1.0 K, the impact of several concentrations (i.e., 50, 100, 200, and 500 ppm) of the plant extracts (ethanol fraction) was examined, as well as the estimated average corrosion rate.

Table 1 displays the corrosion metrics for extracts from Kair (*Capparis decidua*) shrubs, such as surface coverage (θ), inhibition efficiency percentage (IE %), and corrosion rates (mmpy). Additionally, Figure 1 illustrates the relationship between inhibitor concentration and corrosion inhibition effectiveness. The weight loss–time curves for zinc in 0.1 N HCl at various intervals (1, 6, and 24 hours) at 303K temperature, with and without varying amounts of shrub extract, are displayed in the figures. Plots show that compared to an acid solution employed as a blank, the addition of extracts dramatically lowers material loss (g cm^{-2}). Moreover, it was demonstrated that the amount of material loss was concentration-dependent a propensity for all systems under investigation to lose inhibitory efficacy with time. This suggests that some of the inhibitor that has been adsorbed may have desorption from the metal surface (Pramudita *et al*., 2019; Dehghani *et al*., 2020).

Table: 1 Mass Loss measurement (ΔM), Corrosion Rate (mmpy), Inhibition Efficiency (IE %), Surface Coverage (θ) value for use corrosion inhibitors as Shrubs extracts of Kair *(Capparis decidua)* at different concentration (as 50, 100, 200, and 500 ppm) in 0.1 N HCl for duration 1hr, 6hr, 24 hr at 303+ 1.0 K. Area of exposure - 13.0 cm2, Time at and Zn density = 7.14 Mg/m².

Inhibitor Conc.	**Log c**	**Mass Loss(ΔM) mg**			**Inhibition Efficacy (IE %)**			**Corrosion Rate (mmpy)**			**Surface Coverage(θ)**			**log(θ/1-θ)**		
(ppm)		1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr
Blank	0	58	282	514	0.00	0.00	0.00	54.73	44.35	20.21	0.00	0.00	0.00	0	0	0
50	1.698	54	192	364	6.90	31.91	29.18	50.96	30.20	14.31	0.06	0.31	0.29	-0.32	-1.13	-0.38
100	2	29	180	248	50.00	36.17	51.75	27.36	28.31	9.75	0.50	0.36	0.51	-0.24	0.00	0.03
200	2.301	21	158	198	63.79	43.97	61.48	19.81	24.85	7.78	0.63	0.43	0.61	-0.10	0.24	0.20
500	2.698	14	82	124	75.86	70.92	75.88	13.21	12.89	4.87	0.75	0.70	0.75	0.38	0.49	0.49

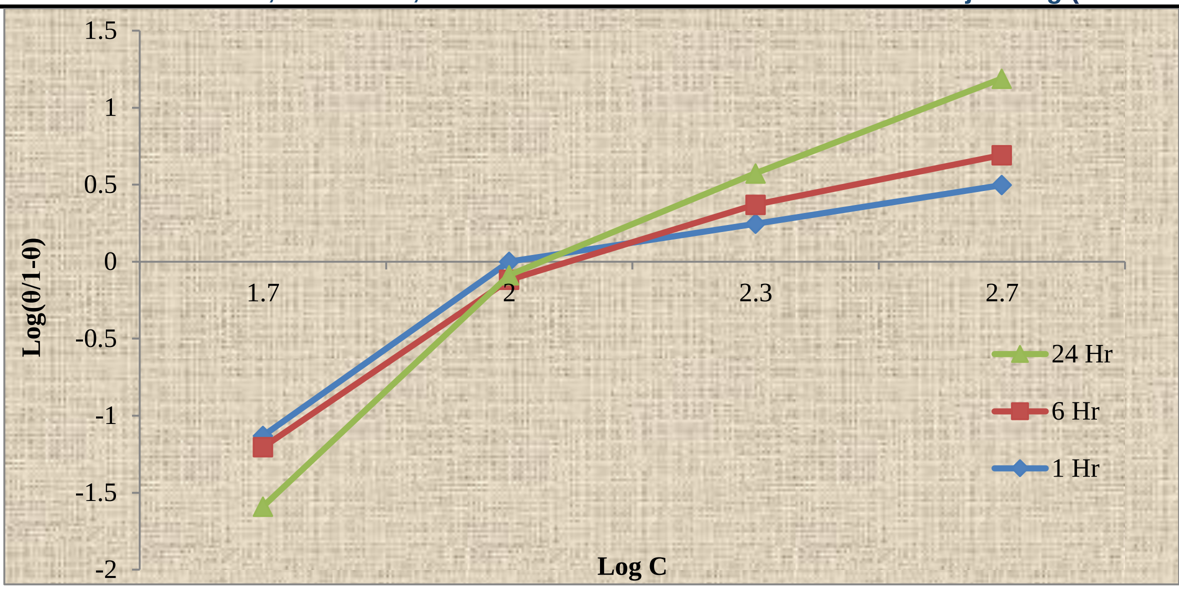

Fig 1 Mass loss curves in between variation of log (θ /1-θ) with log C using Kair *(Capparis decidua)* shrubs extract for Zinc in 0.1 N HCl at 303+ 1.0 K, Time at 1 h, 6 h, 24 hrs.

Table: 2 Mass Loss measurement (ΔM), Corrosion Rate (mmpy), Inhibition Efficiency (IE %), Surface Coverage (θ) value for use corrosion inhibitors as Shrubs extracts of Kair *(Capparis decidua)* at different concentration (as 50, 100, 200, and 500 ppm) in 0.1 N H_2SO_4 for duration 1hr, 6hr, 24 hr at 303+ 1.0 K. Area of exposure - 13.0 cm2, Time at and Zn density = 7.14 Mg/m².

Inhibitor Conc.	**Log c**	**Mass Loss(ΔM) mg**			**Inhibition Efficacy (IE %)**			**Corrosion Rate (mmpy)**			**Surface Coverage(θ)**			**log(θ/1-θ)**		
(ppm)		1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr	1Hr	6Hr	24Hr
Blank	0	82	384	720	0.00	0.00	0.00	77.38	60.40	28.31	0.00	0.00	0.00	0.00	0.00	0.00
50	1.698	56	310	418	31.71	19.27	41.94	52.85	48.76	16.43	0.31	0.19	0.41	-0.33	-0.62	-0.141
100	2	35	278	245	57.32	27.60	65.97	33.03	43.72	9.63	0.57	0.27	0.65	0.12	-0.41	0.28
200	2.301	18	168	188	78.05	56.25	73.89	16.98	26.42	7.39	0.78	0.56	0.73	0.55	0.10	0.45
500	2.698	11	96	110	86.59	75.00	84.72	10.38	15.10	4.32	0.86	0.75	0.84	0.80	0.47	0.74

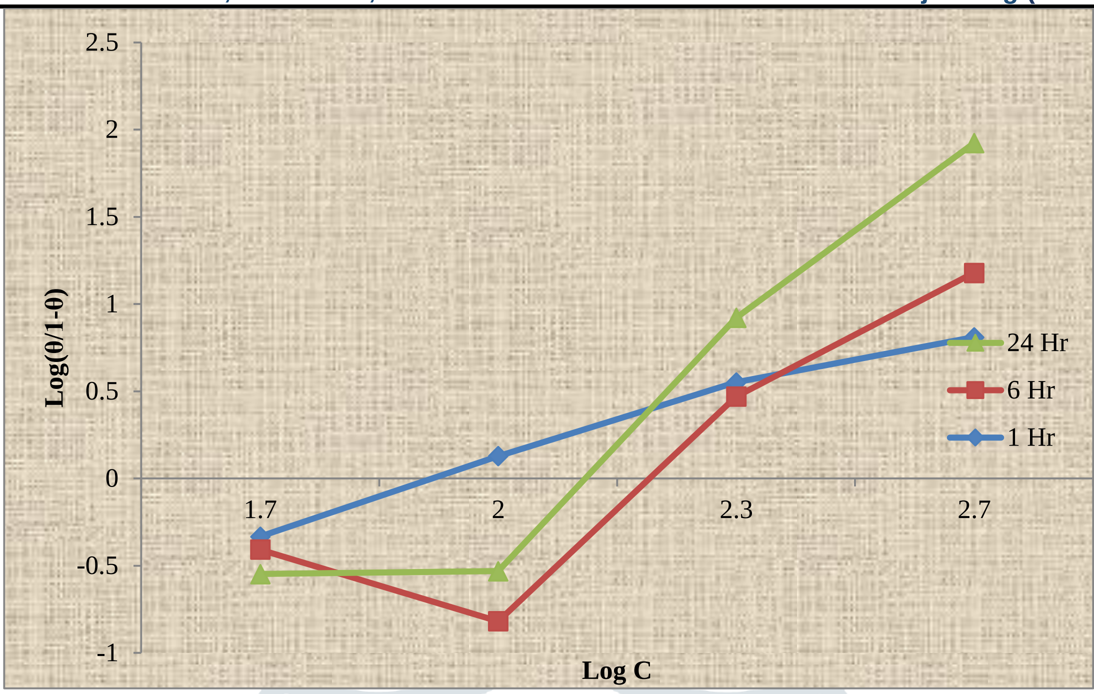

Fig. 2 Mass loss curves in between variation of log (θ /1-θ) with log C using Kair *(Capparis decidua)* shrubs extract for Zinc in 0.1 N H_2SO_4 at 303+ 1.0 K, Time at 1 h, 6 h, 24 hrs.

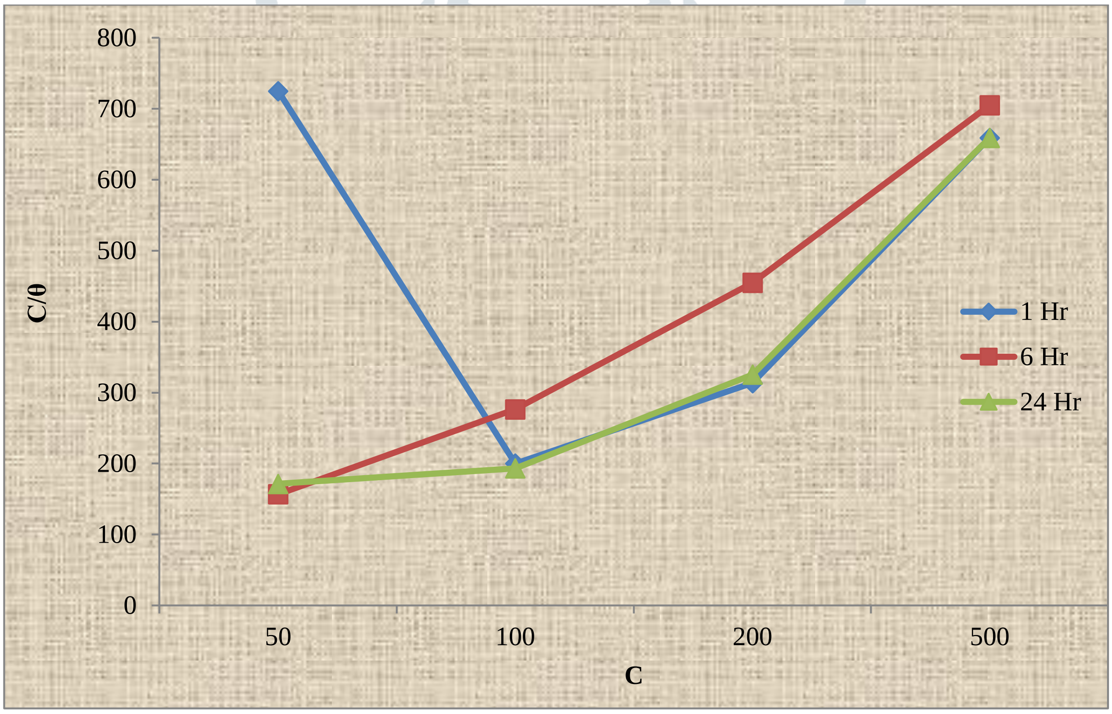

Fig. 3 Mass loss curves in between variation of C/θ with C using Kair *(Capparis decidua)* shrubs extract for Zinc in 0.1 N HCl at 303+ 1.0 K, Time at 1 h, 6 h, 24 hrs.

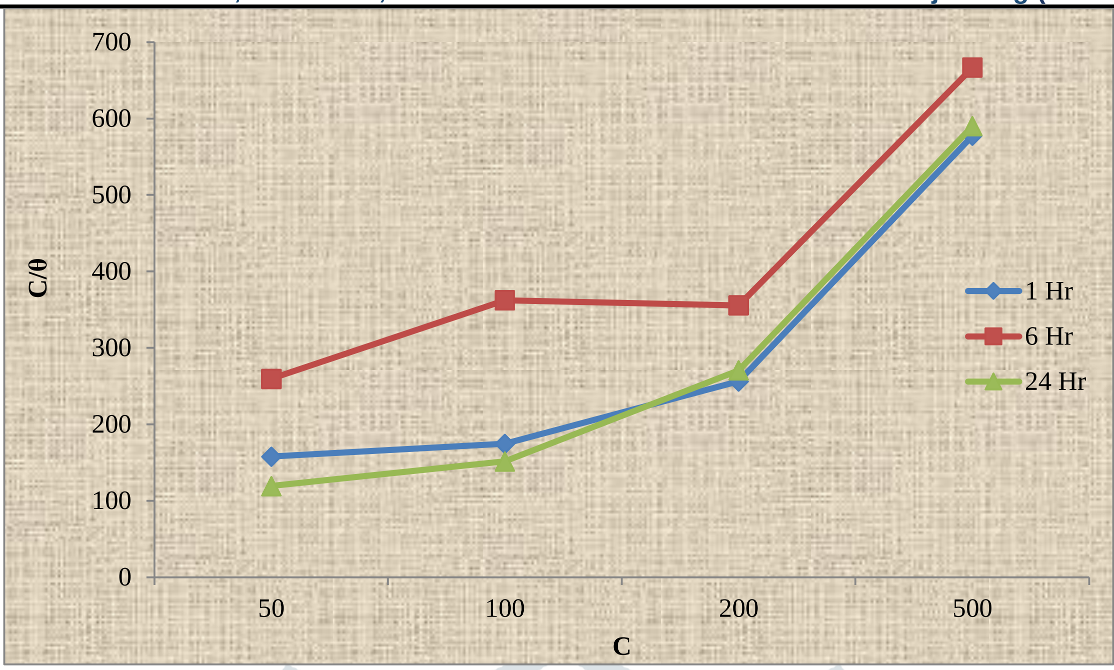

Fig. 4 Mass loss curves in between variation of C/θ with C using Kair *(Capparis decidua)* shrubs extract for Zinc in 0.1 N H_2SO_4 at 303+ 1.0 K, Time at 1 h, 6 h, 24 hrs.

The results of the thermometric approach are presented in the following tables. Increasing temperatures accelerated both weight loss and corrosion, but increasing dosages of the inhibitor (shrubs extract) slowed both. On the other hand, the effectiveness of inhibition decreased with increasing temperatures but increased with increasing extract concentrations. Furthermore, the degree of surface coverage decreased with increasing temperature but increased with increasing inhibitor doses.

Table 3. Comparisons of Inhibition Efficacy (η%) and Corrosion Rate at different temperature in HCl and H_2SO_4 medium using various plants extract.

S. NO.	Inhibitor Concentration	Inhibition Efficacy (η%)	Corrosion Rate (mmpy)	Surface Coverage (θ)	Inhibition Efficacy (η%)	Corrosion Rate (mmpy)	Surface Coverage (θ)	Inhibition Efficacy (η%)	Corrosion Rate (mmpy)	Surface Coverage (θ)
	0.1 N HCl	303K			313K			323K		
1	Blank	0.00	44.36	0.00	0.0	56.65	0.0	0.0	71.56	0.0
2	50	35.46	28.63	0.35	32.49	34.59	0.32	26.66	48.95	0.27
3	100	43.26	25.17	0.43	40.59	30.16	0.41	40.98	32.94	0.41
4	200	57.09	19.03	0.57	48.65	19.65	0.49	34.38	28.84	0.34
5	500	60.99	17.30	0.61	55.56	18.49	0.56	52.65	12.56	0.53

	0.1 N H_2SO_4	303K			313K			323K		
1	Blank	0.00	60.4008	0.0000	0.00	72.15	0.00	0.00	80.48	0.00
2	50	8.33	55.3674	0.0833	9.84	62.65	0.1	10.15	63.56	0.1
3	100	10.16	54.2663	0.1016	10.34	60.65	0.1	20.28	62.92	0.2
4	200	45.31	33.0317	0.4531	31.82	32.65	0.32	27.84	38.51	0.28
5	500	70.05	18.0888	0.7005	61.28	19.62	0.61	50.82	18.56	0.51

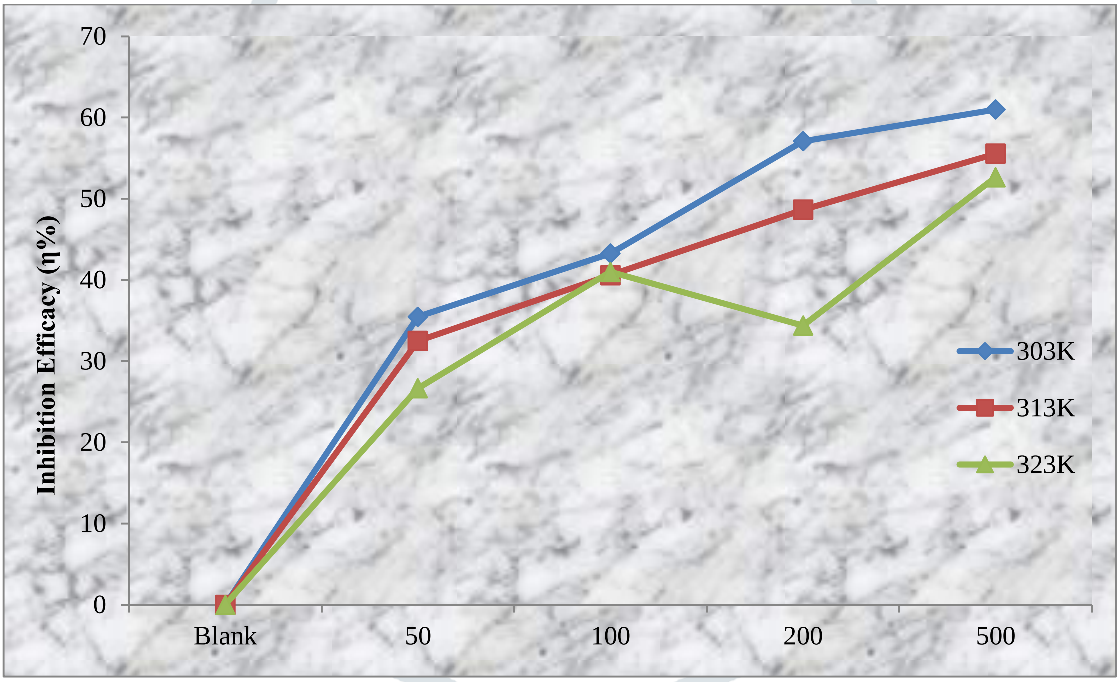

Fig 5 changes in Inhibition Efficacy (η%) with Inhibitor Kair *(Capparis decidua)* shrubs extract Concentration at various temperature in 0.1 N HCl.

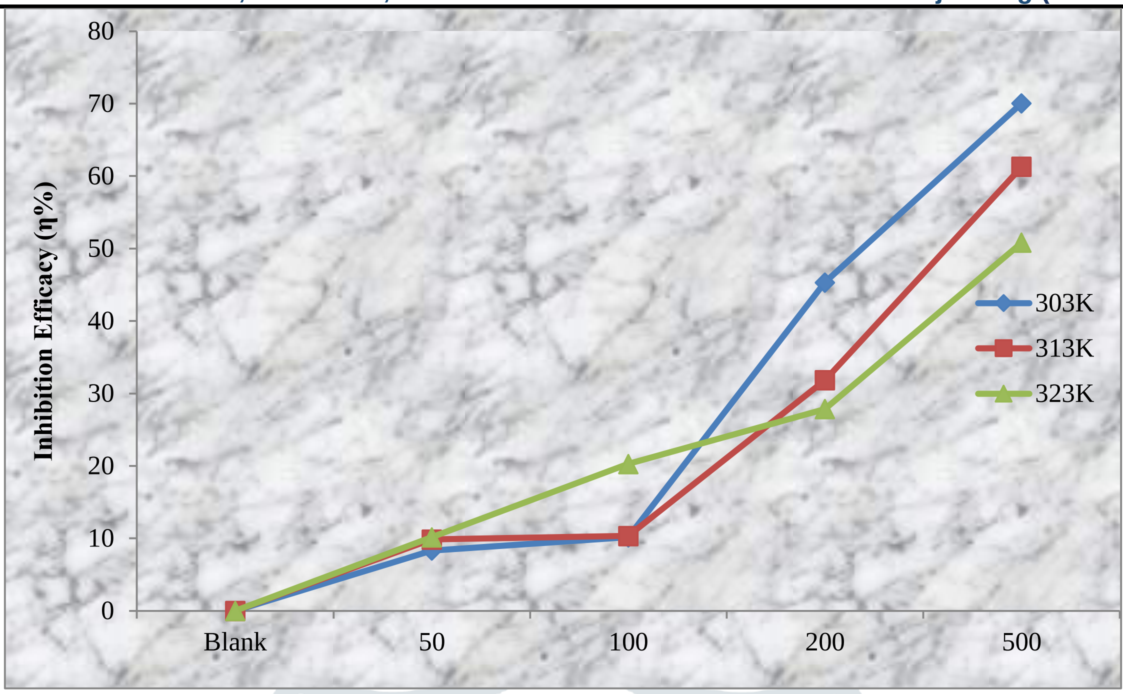

Fig 6 changes in Inhibition Efficacy (η%) with Inhibitor Kair *(Capparis decidua)* shrubs extract Concentration at various temperature in 0.1 N H_2SO_4.

The low entropy and negative enthalpy values of the system, which show a decrease in randomness and increased adsorption of the plant elements, are indications of the exothermic process of corrosion. The spontaneous adsorption of inhibitor molecules on the zinc surface in an acidic media is shown by the negative value of ΔG. The value of -ΔGads is between 20 kJ mol-1 and slightly more than 20 kJ mol-1. Therefore, physisorption are the main causes of inhibitor molecule adsorption on the metal surface (Palaniappan *et al*., 2019; Saxena *et al*., 2018).

Table: 5. Activation parameters for zinc corrosion presence of Kair *(Capparis decidua)* shrubs extract.

Medium	**K_{ads} (ppm^{-1})**	**ΔG_{ads} (KJ/ Mol)**	**-ΔH (KJ/ Mol)**	**ΔS (KJ/ Mol)**
0.1 N HCl	0.022046	-1.855078	7.1142898	0.016803
0.1 N H_2SO_4	0.011563	-15.6548	26.970616	0.136183

The metal surface was completely destroyed in the acid solutions, according to the study, demonstrating that it could not withstand the free acid solutions in the absence of the extract from Kair (*Capparis decidua*) shrubs. The situation changed when an inhibitor was added. The effectiveness of the inhibitor was established by its capacity to protect the surface from damage caused by the molecules of the shrub extract adhering to the active sites of the metal surface and causing some deposition on the metal surface (Kesari *et al*., 2023).

The creation of an association between the lone pairs on the N- and O-atoms of the heterocyclic rings and the zinc surface which involved the displacement of water molecules from the metal surface caused the adsorption of these organic molecules (Cen *et al*., 2024; Kaur *et al*., 2022). The shrub extract from the plant exhibits exceptional inhibitory efficacy as an organic inhibitor when subjected to a range of treatments.

In conclusion, the corrosion inhibition is ascribed to the physical adsorption of the plant's phytochemical components on the metal surface, as indicated by the trend of inhibition efficiency with temperature and the values of activation energy and heat of adsorption that were determined. The values of the thermodynamic and kinetic parameters derived from the experimental data further supported the inhibitory mechanism.

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