



COMPARATIVE EVALUATION OF GREEN CORROSION INHIBITOR ON MILD STEEL CORROSION IN 1 M HCL AND 0.5 M H₂SO₄

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ABSTRACT

The effectiveness of *Persea americana* Seed as a Green Corrosion Inhibitor for Mild Steel in acidic media (1 M HCl and 0.5 M H₂SO₄) was evaluated by weight loss method. The result showed increasing the concentration of seed extract improved its inhibitory efficiency with an optimum concentration 0.5% (V/V) achieving maximum efficiency of 85 % in 1 M HCl and 79 % in 0.5 M H₂SO₄. The best immersion time for maximum inhibition efficiency was found to be 3 h for 1 M HCl and 1 h for 0.5 M H₂SO₄. At 0.5% (V/V) concentration of the inhibitor, the ideal temperature for maximum inhibition efficiency (87%) was 323 K. The study also revealed that the Hydrochloric acid showed synergistic effect whereas Sulphuric acid showed anti-synergistic effect. Adsorption followed Langmuir, Freundlich and Temkin isotherms. The thermodynamic parameters revealed that the inhibition process was spontaneous, exothermic and the interaction between the phytoconstituents and the metal surface took place through physisorption. The probable mechanism has been proposed for the inhibition action and inhibition efficiency follows the order: HCl > H₂SO₄

KEYWORDS: Corrosion inhibitors; Mild steel, Metals Protection, Green Corrosion Inhibitor.

INTRODUCTION

Mild steel corrodes severely when exposed to different acid solution during the acid transportation, descaling, storing acids and other chemical processes.^[1] Despite corroding easily, mild steel remains widely used in construction, transportation, mechanical engineering, and other industries and due to its cost-effectiveness coupled with its reasonable strength.^[2] Sulphuric acid and Hydrochloric acid are widely employed for these rationales. The use of an inhibitor in acid cleaning, pickling, descaling, etching, etc. is a better way to shelter metals against corrosion.^[3] Inhibitors are generally simple to use and provide the impact without seriously affecting the process. Hydrazine, silicates, borates, tungstates, molybdates, pyrrole compounds, arsenates, and chromium (VI), Thiophene, Inorganic compounds (phosphates, chromates, and dichromates) are some of the most effective corrosion inhibitors currently in use.

Their toxic nature and environmental incompatibility pose significant risks to people and the environment.^[4]

Because of the negative impact on the environment, the use of chemical inhibitors has indeed been restricted. In 1932, Arsenic acid was introduced as corrosion inhibitor, which was behind the rise of Well Acidification. However, toxic arsine gas was released from arsenic compounds under acidic environment and many people died as a result of arsenic poisoning in the past. Up until the mid 1970s, Most of the Corrosion Inhibitors used were acids or inorganic salts like arsenate/arsenic acid prior getting succeeded by organic compounds, which often include heteroatoms (N, O, P, or S).^[5] Finding appropriate corrosion inhibitors to substitute harmful and non-biodegradable chemical as well as inorganic substances has been the focus of recent study. This demand is met by chemicals that occur naturally. These are easily accessible, affordable, made of renewable

resources, environmentally friendly, as well as biodegradable.^[6] Plant extracts have become a substitute since they are ecologically tolerable, rapidly available and renewable source.^[7] The current research endeavors to substitute extremely harmful compounds with far less toxic or non-toxic ecologically friendly materials to resist corrosion. Our earlier study findings,^[8-13] discovered a successful implementation of natural substance as an inhibitor in an acidic medium. The ability of the acid extract of *Persea americana* Seed [PAS] to inhibit corrosion as well as the characteristics of the inhibitory effect in 1 M HCl as well as in 0.5 M sulfuric acid have all been investigated, and the findings have been compared.

MATERIALS AND METHODS

2. Experimental

Preparation of the sample

From a big sheet of mild steel, samples measuring 1 x 5 cm² have been cut. The sample specimen had a hole punched into it, which was then manually polished, degreased, cleaned with water, and completely dried and placed in desiccators. By diluting concentrated HCl and

concentrated H₂SO₄ with distilled water, the solution concentrate of 1 M and 0.5 M were obtained. The seeds were taken, air dried in the shade, then pressed into a fine powder. To make the stock solution, 25 g of crushed powder were refluxed separately in 500 mL of 1 M HCl and 0.5 M H₂SO₄ for over 3 hours and left overnight. After filtering, the acid was used to make it up to 500 mL. From prepared stock solution, extracts with varying concentrations ranging from 0.0001% to 0.5% (V/V) were prepared.^[14]

Parameters

- Stock solution: 5%
- Concentration of the inhibitor: 0.015, 0.025, 0.035, 0.045, 0.1, 0.3, 0.5 (% V/V)
- Temperature studied: 30, 40, 50, 60 and ±2 (°C)
- Concentration of the acid: 1 M HCl, 0.5 M H₂SO₄
- Immersion period: 1, 3, 24 and 48 (h)

With varying inhibitor doses, the weight loss technique and higher temperature study was carried out using 0.5 M H₂SO₄ and 1 M HCl as previously described.^[15]

PLANT PROFILE



Figure – 1: *Persea Americana*.

Scientific Name : *Persea americana*

Common Names : Avocado pear, Alligator pear

Tamil Name : Vennai pazham

Origin : Mexico

Family : Lauraceae

Habit : Green-skin, squishy body that can have a pear-, egg-, or spherical form.

3. RESULTS AND DISCUSSION

Weight Loss Measurement

Weight loss studies were used to determine the effectiveness of the PAS extracts at different concentrations in inhibiting the disintegration of mild steel in 0.5 M sulphuric acid and 1 M hydrochloric acid and results are presented in Table – 1 and represented in Figure 2. Table 1 makes it clear that for both 0.5 M and 1 M sulphuric acid, the extract's inhibitory efficacy improved with increasing extract concentration. This

phenomenon could be explained by phytoconstituents adhering to the metal surface. By adhering to the metal surface, the phytochemical constituents block the transfer of mass and charge, keeping the metal surface from corroding.^[16] The level of protection rises as the percentage of the surface that is occupied by molecules that have been adsorbed rises.^[17] The highest efficiency (85%) was recorded at 0.5% (V/V) for 0.5 M sulfuric acid and 79% at 0.050% (V/V) for 1 M hydrochloric acid. Table 1 shows the variance in PAS inhibition effectiveness with immersion time. For 1 M hydrochloric acid and for 0.5 M sulphuric acid, the inhibitory efficiency of the extract was seen to improve up to a certain immersion period before declining further with immersion time. At 3 hours, the highest inhibition efficiency (85%) was reached. The increase in phytoconstituent adsorption with immersion period may be responsible for the rise in inhibition efficiency, and

the decline in inhibition performance may be brought on by the gradual desorption of certain molecules from the mild steel's surface, presenting the surface of the metal to

the corrosive environment. According to the findings, the extract functions successfully as an effective inhibitor in 1 M hydrochloric acid.

Table 1: Inhibition efficiency of different concentrations of the PAS extract in 1 M HCl and 0.5 M H₂SO₄ at various immersion periods.

Acid solution	Conc. of the extract (V/V)	Immersion period in hours / Inhibition efficiency (%)			
		1 h	3 h	24 h	48 h
1 M HCl	0.015	50	34	43	33
	0.025	52	47	54	41
	0.035	61	58	60	46
	0.045	67	62	68	56
	0.1	70	71	75	62
	0.3	76	77	78	65
0.5 M H ₂ SO ₄	0.5	81	85	82	69
	0.015	44	33	30	29
	0.025	47	39	37	40
	0.035	59	46	44	46
	0.045	76	52	48	50
	0.05	79	58	51	57

Figure – 2

Inhibition efficiency of different concentrations of the PAS extract in 1M hydrochloric acid and 0.5 M sulphuric acid at various immersion periods.

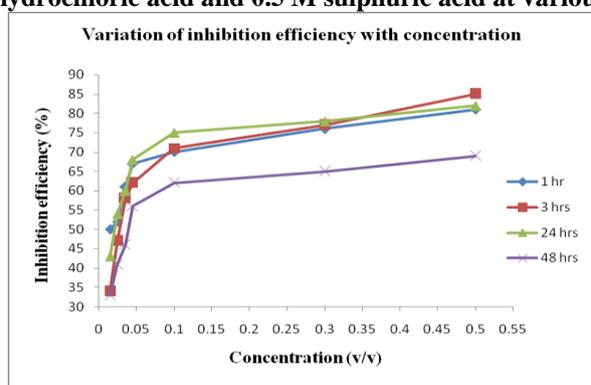


Figure – 2 (a)

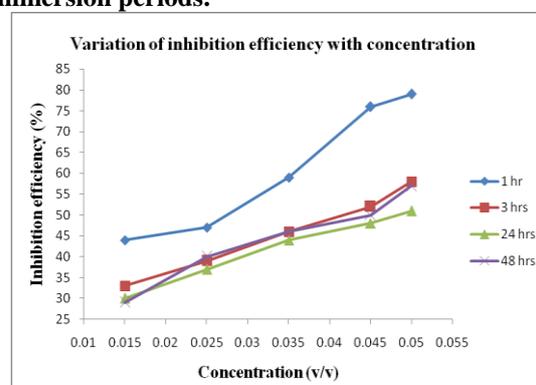


Figure –2 (b)

Temperature study

The findings of an experimental investigation on the impact of temperature upon mild steel deterioration with varying concentrations of the extract of PAS in hydrochloric acid are described in Table 2, shown in Figure 3. The efficacy of the inhibition enhanced from 313 K to 323 K and then declined as the temperature rose further. The extract molecules may well have desorbed from the surface of the mild steel at 333 K after adsorption up to 323 K, which would explain the drop in efficiency at that temperature.^[17] At a 0.5% (V/V) concentration of the extract, the ideal temperature for maximum effectiveness (87%) is 323 K. The

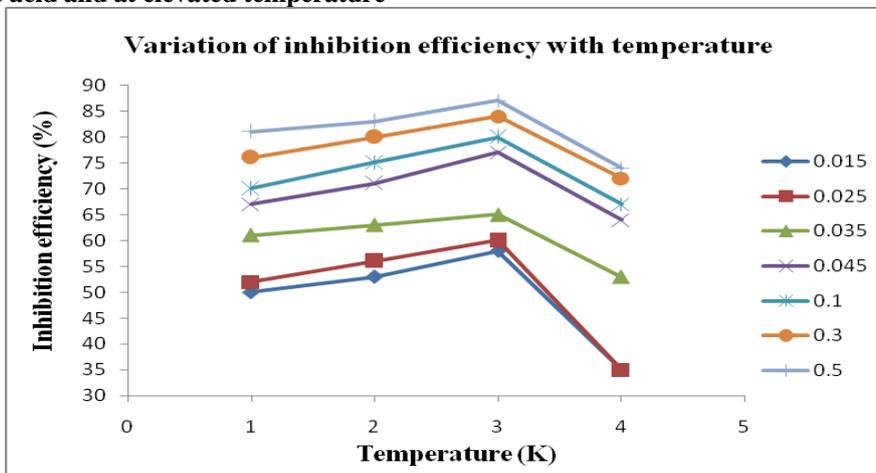
disintegration of mild steel and the substantial desorption of the inhibitor from metal surface due to change in temperature may compete, causing an inconsistency in the values of inhibition efficiency indicated in Table 2 and Figure 3. At room temperature, a trend can be seen in the prevention of mild steel corrosion by PAS in 0.5 M H₂SO₄. Anti- synergistic effect is observed only at higher temperature. At elevated temperature, the PAS extract employed in 0.5 M sulphuric acid enhances the rate of corrosion and thereby reducing inhibition efficiency. Therefore, due to this effect the further studies have not been carried out in sulphuric acid media.

Table – 2: Inhibition efficiency of different concentrations of the PAS extract in 1 M hydrochloric acid and at elevated temperature

Conc. of the extract (% V/V)	Temperature (K) and Inhibition efficiency (%)			
	303	313	323	333
0.015	50	53	58	35

0.025	52	56	60	35
0.035	61	63	65	53
0.045	67	71	77	64
0.1	70	75	80	67
0.3	76	80	84	72
0.5	81	83	87	74

Figure – 3
Inhibition efficiency of different concentrations of the PAS extract in 1 M hydrochloric acid and at elevated temperature



Adsorption isotherm

The adsorption characteristic of the extract is assessed by plotting surface coverage against inhibitor concentration using typical adsorption isotherms: Langmuir (figure –

4), Freundlich (figure – 5), and Temkin isotherms. (figure – 6). Each isotherm has the same general equation: $F(\theta, x) \exp(-2a\theta) = kc$

Type of Isotherm	Plot
Langmuir	$\log \theta / 1 - \theta$ vs. $\log C$
Freundlich	$\log \theta$ Vs $\log C$
Temkin	θ Vs $\log C$

Figure – 4
Langmuir adsorption isotherm for the dissolution of mild steel in 1M hydrochloric acid in the absence and presence of various concentrations of PAS extract.

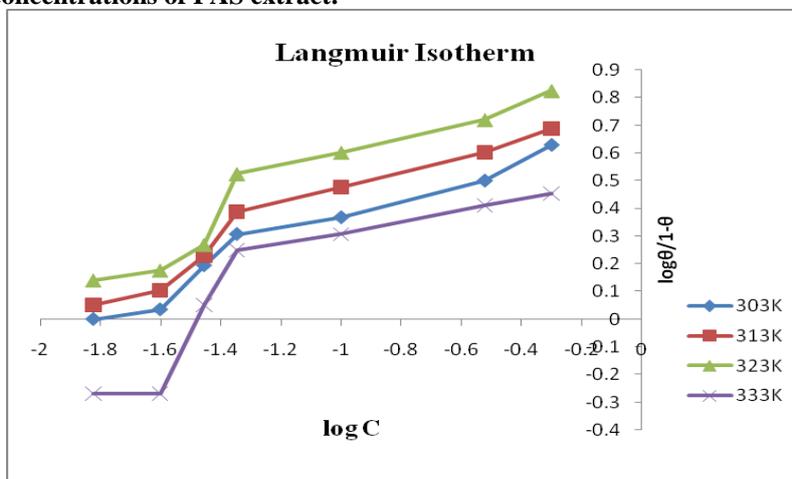


Figure – 5.

Freundlich adsorption isotherm for the dissolution of mild steel in 1 M hydrochloric acid in the presence and absence of various concentrations of PAS extract

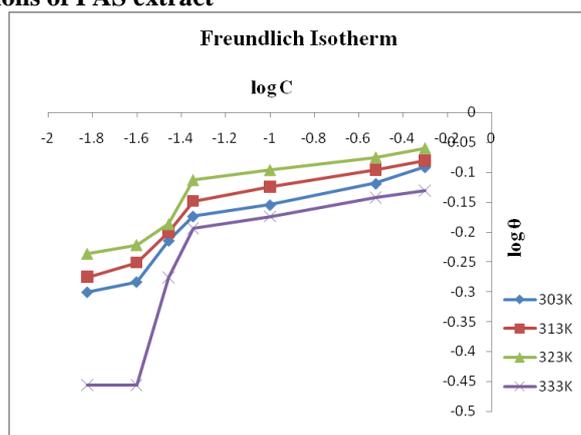
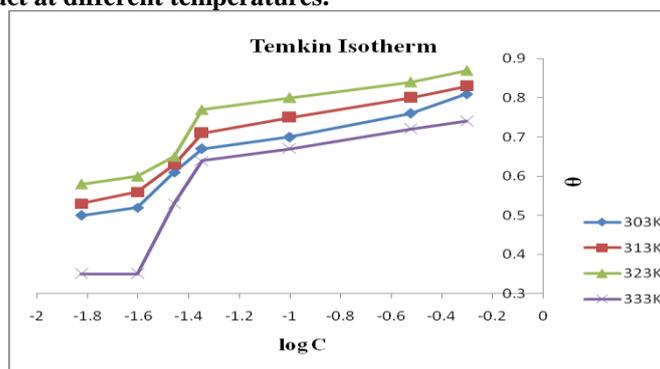


Figure – 6

Temkin adsorption isotherm for the mild steel dissolution in 1M hydrochloric acid in the presence of various concentration of PAS extract at different temperatures.



“The applicability of Temkin isotherm verifies the assumption of monolayer adsorption on a uniform homogeneous metal surface with an interaction in the adsorption layer”^[18]

Thermodynamic functions

The Table - 4 shows the Arrhenius equation and Transition State Equation-derived thermodynamic values

Figure – 7

Arrhenius plot for the dissolution of mild steel in 1M hydrochloric acid in the presence and absence of various concentrations of PAS extract at different temperatures.

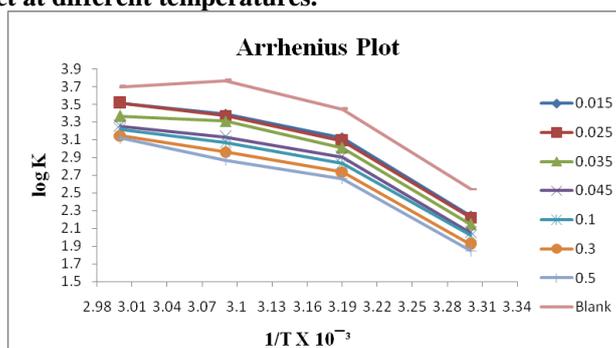
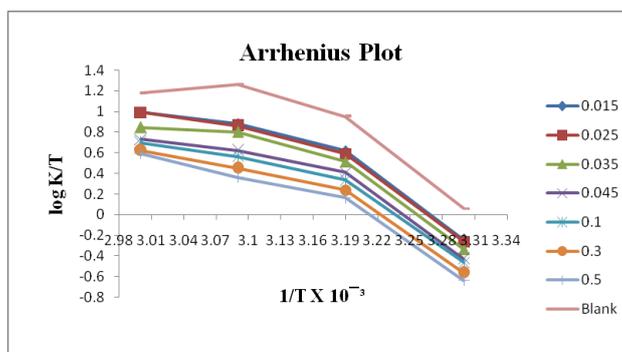


Figure – 8: Arrhenius plot for the dissolution of mild steel in 1M hydrochloric acid in the presence and absence of various concentrations of PAS extract at different temperature.

From Figure-8, the entropy and enthalpy values has been calculated



From the Figure-7, the activation energy has been calculated using the formula, slope = $-2.303 E_a/RT$

Activation parameters

The activation energy, adsorption entropy, and adsorption enthalpy of pure 1 M hydrochloric acid with

the addition of different PAS extract amounts are shown in Table 3.

Table – 3: Activation parameters for the dissolution of mild steel in 1 M hydrochloric acid in the presence and absence of various concentration of PAS extract.

Concentration of the extract (V/V)	$-E_a$ kJ / mol	$-\Delta H_{ads}$ kJ / mol	ΔS_{ads} J / K / mol
Blank	74.2	77.0	-55.2
0.015	79.6	78.4	-59.5
0.025	81.0	74.7	-46.2
0.035	77.3	71.8	-34.7
0.045	74.4	71.9	-34.0
0.1	74.5	73.1	-36.1
0.3	75.7	75.3	-41.8
0.5	77.9	71.6	-44.4

The phytochemical constituents of an extract's adhesion to mild steel's surface are consistent well with E_a 's negative values. The difference between the activation energy in the presence of the extract and in its absence suggests that a physical adsorption layer has formed. The extracts' constituents are adsorbing by an exothermic process, as shown by the negative sign of enthalpy.^[19] Entropy's negative value denotes a drop in entropy that occurs throughout the adsorption mechanism. The extracts' constituent parts initially had unrestricted

movement when they were adsorbing to the mild steel surface, but as the adsorption process advanced, the components were orderly adsorbed into the surface of mild steel, resulting in a decline in entropy.^[20] The fact that the free energy is negative suggests that physisorption is the mechanism through which inhibition occurs. The durability of the adsorbed layer and the spontaneity of adsorption are both highlighted by the negative free energy values.^[21]

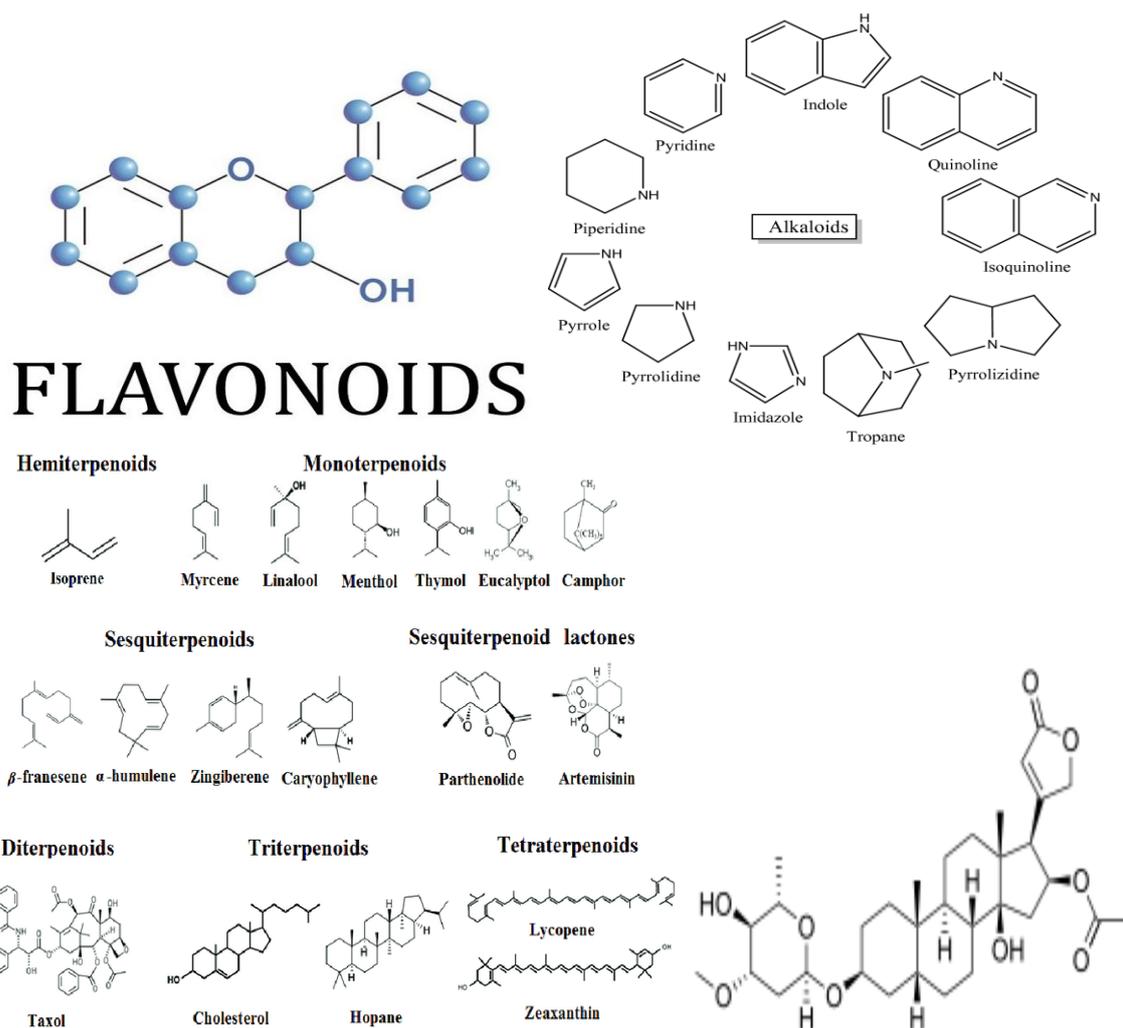
Table – 4

Thermodynamic functions for the dissolution of mild steel in 1 M hydrochloric acid in the presence and absence of various concentrations of PA extract at various temperature.

Concentration of the extract (% V/V)	$-\Delta G_{ads} KJmol^{-1}$			
	303 K	313 K	323 K	333 K
Blank	15.85	21.79	24.48	24.79
0.015	14.1	20.05	22.12	23.62
0.025	13.98	19.63	22.03	23.62
0.035	13.55	19.18	21.65	22.68
0.045	13.01	18.56	20.54	21.95
0.1	12.82	18.1	20.16	21.73
0.3	12.23	17.53	19.49	21.26
0.5	11.8	17.08	18.92	21.08

Probable Mechanism

The major phytoconstituents present in PAS are: Flavonoids, Alkaloids, Terpenoids, Glycosides, Coumarins.



Glycosides

The major functional present in these phytoconstituents are hydroxyl groups, hetero atoms, amino groups, oxygen containing hydrocarbons and carbon double bonds. These functional groups may be the cause of the inhibition. These functional groups either become adsorbed on the surface of metal or it is involved in the bond formation and thereby preventing the mild steel exposure to the corrosive environment.

“Hydrochloric acid is found to have more inhibition efficiency than Sulphuric acid”. This is because, chloride ions were found to have a strong absorption tendency than sulfate ions.^[22]

SUMMARY AND CONCLUSION

The results obtained during this investigation have been summarized: The acid extract of PAS brought out a maximal inhibitory effectiveness of 85 % and 79 % in 1 M HCl in 0.5 M H₂SO₄, respectively. According to the research performed, the effectiveness of the inhibition rises as the concentration does. The ideal concentration for maximum efficiency (85% and 79%) was found to be 0.5% (V/V) in both mediums using the mass loss technique at room temperature. The optimum period of immersion for maximum inhibition efficiency was

observed as 3 hrs (1 M HCl) and 1 hr (0.5 M H₂SO₄). At 0.5% (V/V), 323 K was determined to be the ideal temperature for achieving the highest level of inhibition efficiency (87%). The study also revealed that the hydrochloric acid shows synergistic effect whereas sulphuric acid shows anti-synergistic effect. The adsorption kinetics was carried out using Langmuir, Freundlich and Temkin adsorption isotherms. The thermodynamic properties indicated that physisorption was the mechanism by which the phytoconstituents interacted with the metal surface and that the inhibitory action may have been exothermic and spontaneous. The probable mechanism has been proposed for the inhibitory action. “Hydrochloric acid is found to have more inhibition efficiency than Sulphuric acid”.

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