

One-Pot, Eco Sustainable Synthesis, Spectral Studies and Corrosion Inhibition of Mild Steel in different concentrations of H₂SO₄ solution by 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide Schiff Base

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Abstract

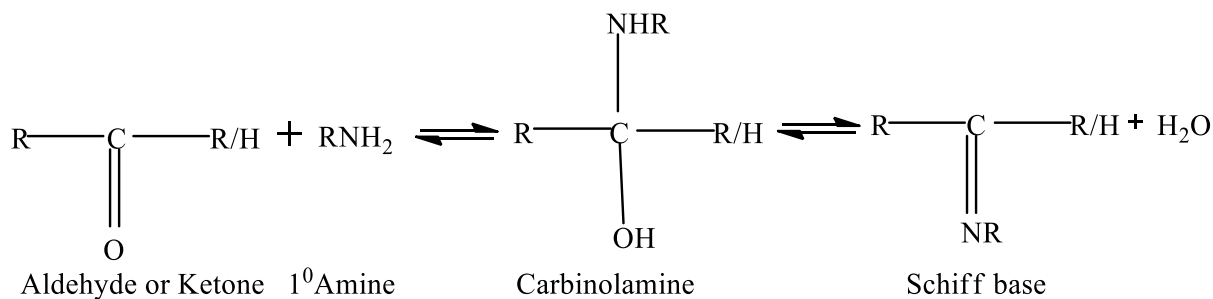
The Schiff base 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide generated from Gallic acid hydrazide and 4-hydroxy-3-methoxy benzaldehyde by microwave induced irradiation. Reaction showed enhanced yield and less time, easier workup. The characterization of synthesized molecule has been done on the basis of elemental, spectral (FTIR, ¹HNMR, Mass) analyses and surface morphology by Scanning Electron Microscopic (SEM). The structural composition of synthesized compound have been determined by X-Ray diffraction (XRD). The inhibitive property of Schiff base on the corrosion of mild steel strip in different concentrations (0.5N, 1N, 2N) of H₂SO₄ were studied using weight loss technique. Absorption of the inhibitor Schiff base 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide on mild steel strip surface was consistent with the Langmuir isotherm.

Keywords: Microwave irradiation, SEM, XRD, Corrosion inhibition, Mild steel.

INTRODUCTION

Schiff bases (SBs) are widely used in inorganic, organic and analytical chemistry. They have been applied as dyes, catalysts, polymer stabilizers, luminescence chemosensors, and have been recommended for solar energy applications[1]. In addition, the synthesis of SB is necessary for a number of pharmacological and biological uses, such as antimalarial, anti-proliferative, antiviral, analgesic, antibacterial, anti-inflammatory, antipyretic, and antifungal.[2-3].

These implications have contributed to the development of several synthetic techniques for the manufacture of Schiff bases. The first synthesis of Schiff bases (imines) was documented by Hugo Schiff in the 19th century. A Schiff base is regarded as an aldehyde with C=N group (an azomethine -N=CH- group) rather than a C=O group.[4] Typically, it is created when primary amines react with aldehyde. Schiff bases are typically created by the nucleophilic attachment of the NH₂ group to the C=O of the aldehyde under azeotropic refluxing conditions, generating a carbinolamine molecule with the simultaneous elimination of water, which dehydrates to produce an imine. [5]



The microwave-assisted synthesis process is more eco-friendly than traditional thermal synthesis. Lower yields and a longer setup time were the results of thermal synthesis, whereas microwave-assisted synthesis offers advantages, including improved conversion and less waste with a decent yield of Schiff base.[6] Since it is less complicated, more accurate, more affordable, and simpler to establish than conventional methods, it is a useful technique in organic synthesis.

Due to the presence of imine groups (>C=N-) and electronegative nitrogen, in the molecules, Schiff bases have the greatest advantage of being able to be conventionally and easily synthesised from relatively inexpensive starting material.[7] Although proton transfer is recognised to be essential for the physicochemical properties and useful applications of Schiff base.[8] Schiff bases are also cost-effective inhibitors of the corrosion of steel in acidic media. Additionally, because the majority of chemical substances used to stop the corrosion of metals and alloys are poisonous and hence dangerous to human health and the environment, so their use is restricted.[9] The carbon-nitrogen double bond (azomethine group) of Schiff bases plays a significant role in synthetic reactions in organic chemistry. Mild steel is the most widely used construction materials and in the manufacturing of installation for petroleum industries. Various environmental factors like acids, acidic rain water, temperature variation and moisture could seriously affect the durability of the mild steel[10]. The mild steel corrosion has become important particularly in acidic media because of the increased industrial application of acid solutions. The corrosion inhibitors are the chemical substance which decrease the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agents [11].

Result and Discussion

Synthesis

A reaction mixture of 0.01 mol of gallic acid hydrazide reacts or 3,4,5-trihydroxy benzohydrazide in water, 0.01 mol of 4-hydroxy-3-methoxy benzaldehyde and 2 drops of Conc.H₂SO₄ was incubated inside a microwave oven running at 160 W for 7-8 minutes. The reaction mixture was placed into water when the reaction completed and it cooled at room temperature. The resultant solid proceeds to recrystallization. TLC checked on the reaction's progression every two minutes.[12] After some time, TLC revealed a complete conversion. The TLC spots were found using UV light at 254 nm, and H₂SO₄ in ethanolic solution (5%, v/v) was sprayed on before being heated to 100 °C.[13] By the condensation reaction to afford the desired schiff base (3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide was obtained.(Scheme-I).The physical and analytical data of schiff base 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide is shown in Table-I.

In the IR spectra of 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide (Schiff Base) characteristic absorption due to >C=N- group appears at 1630-1620 cm⁻¹. -NH- absorption appears as a broad band from 3250-3180 cm⁻¹. The vibration bands at 1500-1400, 1100-1050, and 900-700 cm⁻¹ shows the presence of aromatic ring in the Schiff base.

In the ¹H NMR Spectra of Schiff Base 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide -CH=N- proton resonance signal appears as a sharp singlet at δ 8.2 ppm. This up field confirms the conversion of formyl group (-CHO) into imino group(-CH=N-). Aromatic Proton signals appears as multiplates at δ7.2-7.5 ppm. Final confirmation is obtained by the fast atomic bombardment (FAB) mass spectra as M⁺ at 422 that corresponds to their molecular mass which is C₁₉H₃₈N₂O₈ respectively.

X-Ray powder Diffraction (Figure-I) of synthesized Schiff base showed that crystalline nature and average size of grain were 37-58nm. Scanning Electron Microscopy (SEM) image (Figure-II) of synthesized base detected the existence of microscopic grains with non-uniform, size and managed morphological agglomeration.

The percentage of inhibition efficiency and surface coverage obtained from weight loss method at different concentrate of inhibitor for the corrosion of Schiff base in 0.5N, 1N, 2N H₂SO₄ for an immersion period of 1hour, 6 hours,24 hours at 298+0.1K, area of exposure 7.7cm² are shown in Table III, IV and V. The results show that inhibitor actually inhibited the corrosion of mild steel in 0.5N, 1N, 2N H₂SO₄ at constant temperature (298+0.1K) the IE% increases with increasing inhibitor concentration. This behaviour is the result of increased adsorption oh the inhibitor on the meal surface. The inhibition efficiency (IE %) and degree of surface coverage (θ) were calculated using these equations (i) & (ii) respectively [14].

$$IE (\%) = (W_u - W_i)/W_u \times 100 \quad \dots\dots\dots(i)$$

$$\theta = (W_u - W_i) / W_u \quad \dots\dots\dots(ii)$$

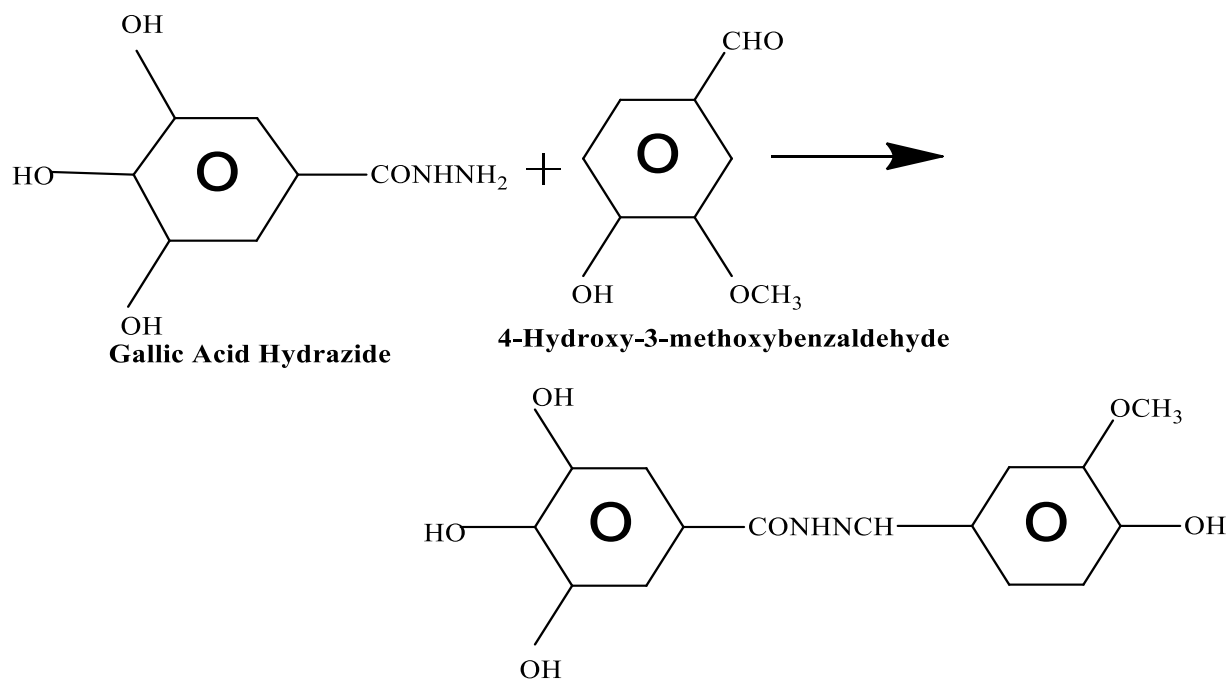
Where W_u and W_i are the weight loss of mild steel in 0.5N, 1N, 2N H₂SO₄ in absence and presence of Schiff base. The degree of surface coverage using Langmuir adsorption isotherm. The assumption of Langmuir adsorption isotherm can be expressed as Equation (iii)

$$C/\theta = 1/k + C \quad \dots\dots\dots (iii)$$

Where C is the concentration of the inhibitors, θ is the degree of surface coverage of the inhibitor (3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide) and k is the adsorption equilibrium constant. Taking logarithm of equation (iii).

$$\log C/\theta = \log C - \log k \quad \dots\dots\dots (iv)$$

Figure - III, IV, V, VI, VII & VIII shows Langmuir adsorption isotherm for the adsorption of Schiff 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide on the mild steel strip surface. Valves of adsorption parameters deduced from the isotherm are given in the Table III, IV and V. From the results obtained, it is significant to note that these plots are linear with the slopes equal to the unity, which indicates a strong adherence of the adsorption data to the assumption establishing Langmuir adsorption isotherm. As we can see from Figure III, IV, V, VI, VII & VIII of 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide inhibitor was found to have the best fit of Langmuir adsorption isotherm.



3,4,5-trihydroxy-N-(4-hydroxy-3-methoxybenzylidene) benzohydrazide (SB)

Scheme-I

Table -I: The Physical and Analytical Data of 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide Schiff base

Molecular formula	Exact Mass	Molecular weight	M.P.(°C)	Yields %	Elemental Analysis Found (Calculated) %			
					C	H	N	O
C ₁₉ H ₃₈ N ₂ O ₈	422.26	422.51	254	89.36	54.01 (54.00)	9.07 (9.06)	6.63 (6.60)	30.29 (30.28)

Table -II: Spectral analyses of 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide Schiff Base

Molecular formula	IR(KBr) ν_{\max} cm ⁻¹ .	¹ H NMR(CDCl ₃) δ ppm	Mass (m/z)	XRD
C ₁₉ H ₃₈ N ₂ O ₈	1630-1620cm ⁻¹ (>C=N-Str. mode) 1500-1400,1100-1050 & 900-700 cm ⁻¹ (Aromatic C-H),3250-3180 cm ⁻¹ (-NH- str.)	8.2(S, CH=N,1H), 7.2-7.5(sm,Ar-H,3H)	422.26(M ⁺)	37-58nm (Average Size of Grains)

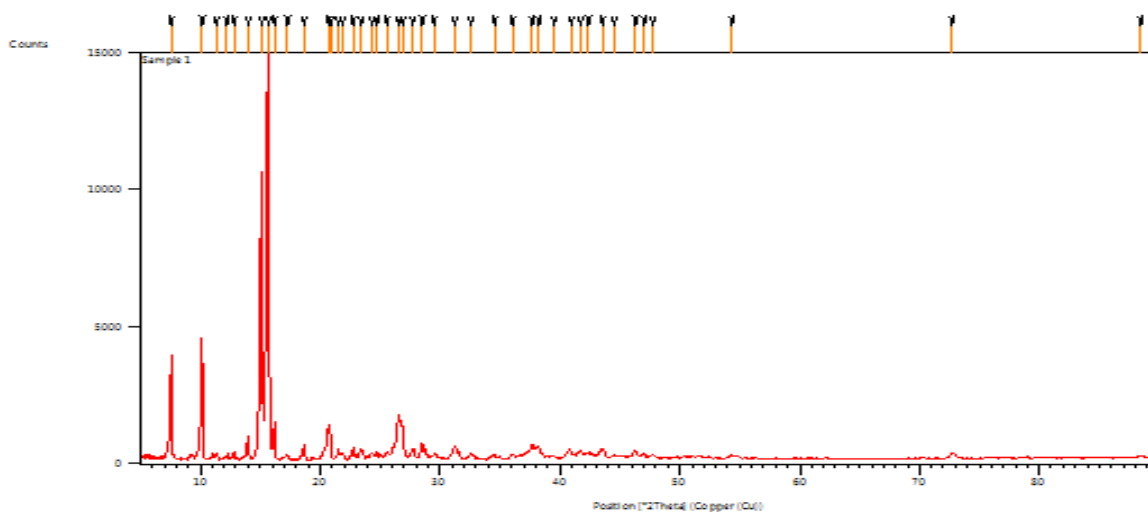


Figure I: XRD pattern of Schiff Base 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide

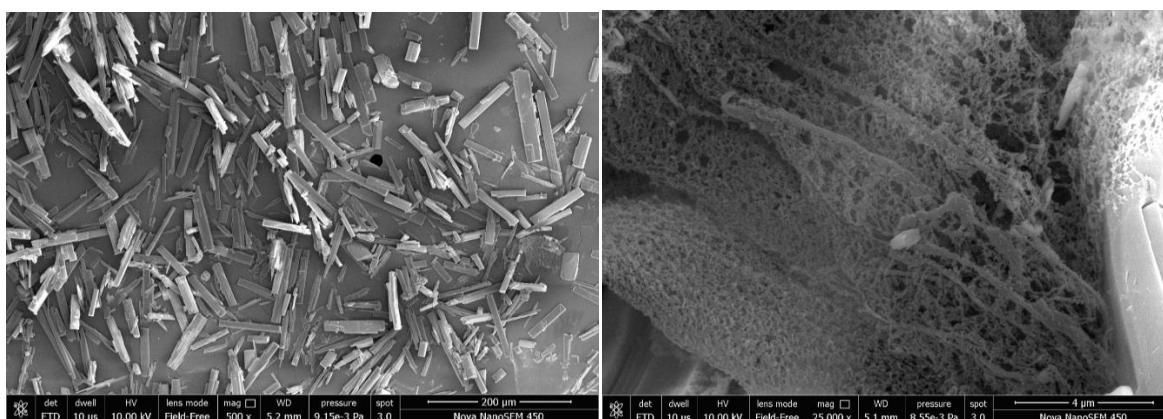


Figure II: SEM image of Schiff base 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide

Experimental

All the melting point were determined in open capillary tubes and are uncorrected. The FT IR Spectra (ν_{\max} cm^{-1}) were recorded on a Perkin Elmer 557 grating infrared spectrophotometer in KBr pallets. PMR spectra were recorded on Bruker Spectrometer (200MHz) using CDCl_3 as a solvent. TMS was used as internal standard (chemical shift in δ ppm). Mass spectra were recorded on kratos 30 and 50 mass spectrometer. A domestic microwave oven (LG, MS-194A) operating at 2450MHz (40 % power ,320 W) was used in the experiment- X-ray powder diffraction(XRD) is efficient and used to determine the phase and cell dimension of crystalline compounds. The Schiff base under investigation was finely powdered, homogenised and the bulk composition was calculated on an average. The purity of the compound was checked by TLC using silica Gel-G as adsorbent, UV light or iodine accomplished visualization 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide Schiff base was prepared by the literature method [15]. The used all chemicals for the preparation of Schiff base were AR grade (MERCK).

Investigation on X-Ray powder diffraction were examined at from an angle of 100 to 800. The range of the powder XRD patterns is $2\theta=0-80^\circ$. Scherrer's formula was used to determine the Schiff bases' average crystalline size.[16] In XRD X-axis shows the pattern is measured in 2θ and Y-axis is relative intensity of the diffracted beam. $d_{\text{xrd}}=0.9\lambda/\beta \cos \theta$

Scanning Electron Microscopy (SEM) is used to give the information of the surface topography, crystalline structure, chemical and electrical behaviour of Schiff bases.[17] The corrosion rate (ρ), inhibition efficiency (IE%), mass loss (ΔM), surface coverage (θ) determined from weight loss method. [18]

Conclusion:

The 3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide inhibits the corrosion of mild steel in different concentrations of H₂SO₄ solutions with inhibition efficiency of 84.86% (0.5N H₂SO₄), 80.35%(1N H₂SO₄),77.02% (2N H₂SO₄) of 0.5 %v/v of Schiff base concentration for 24-hour exposure time, which are effective in reducing corrosion of the mild steel strip at temperature of 298+0.1K. The adsorption of the inhibitor Schiff base was consistent with the Langmuir adsorption isotherm. The inhibitor molecule (3,4,5-trihydroxy-N-(4-hydroxy-3-methoxy benzylidene) benzo hydrazide) adsorbed on the metal surface and tend to retard the rate of corrosion by reducing the number of available sites for corrosion.

Table III: - Mass Loss measurement (ΔM), Corrosion Rate(ρ) (mmpy), Inhibition Efficiency ($\eta\%$), Surface Coverage(θ) of Schiff's bases inhibitors for mild steel in 0.5N H₂SO₄ at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm²

Inhibitor Concentration (%) (w/v)	Mass Loss (ΔM)			Inhibition Efficiency($\eta\%$)			Surface Coverage(θ)			log($\theta / 1-\theta$)			log c	log(c/ θ)			Corrosion Rate(ρ)		
	1h	6h	24h	1h	6h	24h	1h	6h	24h	1h	6h	24h		1h	6h	24h	1h	6h	24h
-	92	134	185	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-				22.0	32.1	44.3
0.1	50	64	73	45.65	52.24	60.54	0.4565	0.5224	0.6054	0.0757	0.0389	0.1859	-1.00	0.6595	0.7161	0.779	15.3589	11.9992	17.5188
0.2	26	56	44	71.74	58.21	76.22	0.7174	0.5821	0.7622	0.4046	0.1439	0.5058	-0.698	0.5538	0.4615	0.579	6.2396	13.4391	10.5593
0.3	23	34	35	75.00	74.63	81.08	0.7500	0.7463	0.8108	0.4771	0.4685	0.6320	-0.522	0.3971	0.1307	0.4305	5.5196	8.1594	8.3994
0.5	20	27	28	78.26	79.85	84.86	0.7826	0.7985	0.8486	0.5563	0.5980	0.7487	-0.301	0.1931	0.1987	0.2298	4.7997	6.4796	6.7195

Table IV: - Mass Loss measurement (ΔM), Corrosion Rate(mmpy), Inhibition Efficiency ($\eta\%$), Surface Coverage(θ) of Schiff's bases inhibitors for mild steel in 1.0N H₂SO₄ at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm²

Inhibitor Concentration (%) (w/v)	Mass Loss (ΔM)			Inhibition Efficiency($\eta\%$)			Surface Coverage(θ)			log($\theta / 1-\theta$)			log c	log(c/ θ)			Corrosion Rate(ρ)		
	1h	6h	24h	1h	6h	24h	1h	6h	24h	1h	6h	24h		1h	6h	24h	1h	6h	24h
-	86	104	173	0.0	0.0	0.0	0.0	0.0	0.00	-	-	-	-				20.63	24.95	41.51
0.1	42	50	72	51.1	51.9	58.3	0.511	0.519	0.5838	0.0202	0.0334	0.1470	-1.00	0.709	0.7154	0.766	10.07	11.99	17.27
0.2	36	43	60	58.1	58.6	65.3	0.581	0.586	0.6532	0.1427	0.1519	0.2749	-0.698	0.462	0.4663	0.513	8.63	10.31	14.23
0.3	29	38	51	66.2	63.4	70.5	0.662	0.634	0.7052	0.6628	0.2935	0.3788	-0.522	0.3434	0.3246	0.370	6.95	9.11	12.23

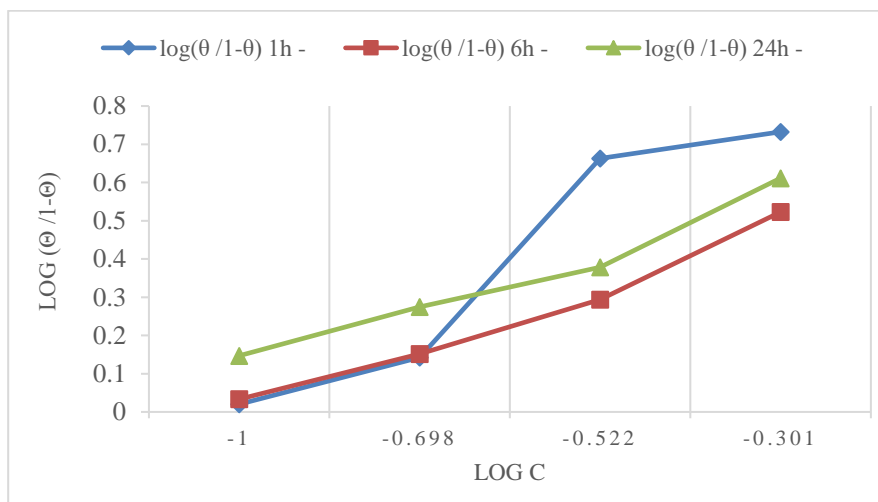


Figure IV: -Variation of $\log(\theta / 1-\theta)$ with $\log c$ for Schiff's bases inhibitors for mild steel in 1.0N H₂SO₄ at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure- 7.75cm²

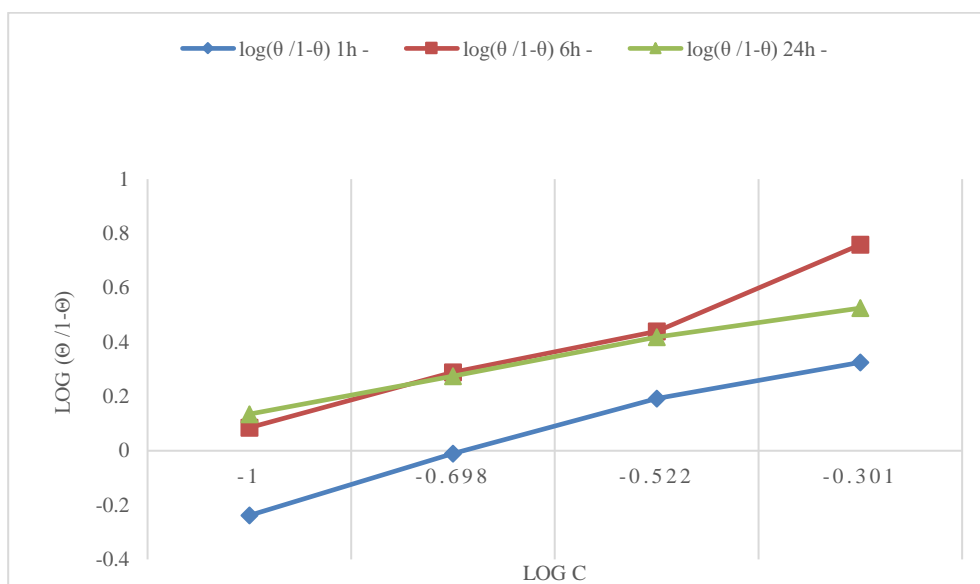


Figure V: -Variation of $\log(\theta / 1-\theta)$ with $\log c$ for Schiff's bases inhibitors for mild steel in 2.0N H₂SO₄ at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm²

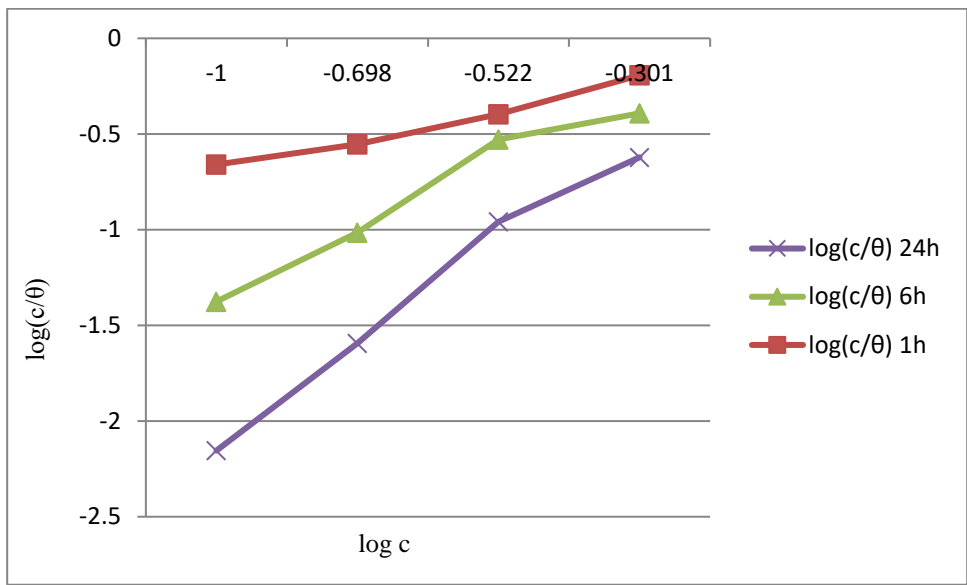


Figure: -VI: - Variation of $\log(c/\theta)$ with $\log c$ for Schiff's bases inhibitors for mild steel in 0.5N H2SO4 at 298+ 0.1K, Time at 1h,6h,24h,Area of exposure - 7.75cm²

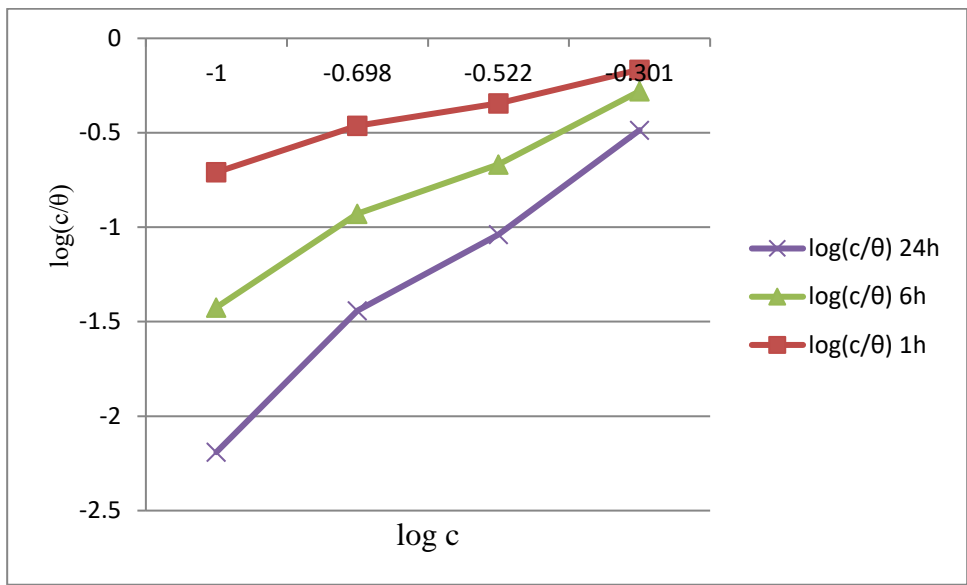


Figure VII: - Variation of $\log(c/\theta)$ with $\log c$ for Schiff's bases inhibitors for mild steel in 1.0N H2SO4 at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm²

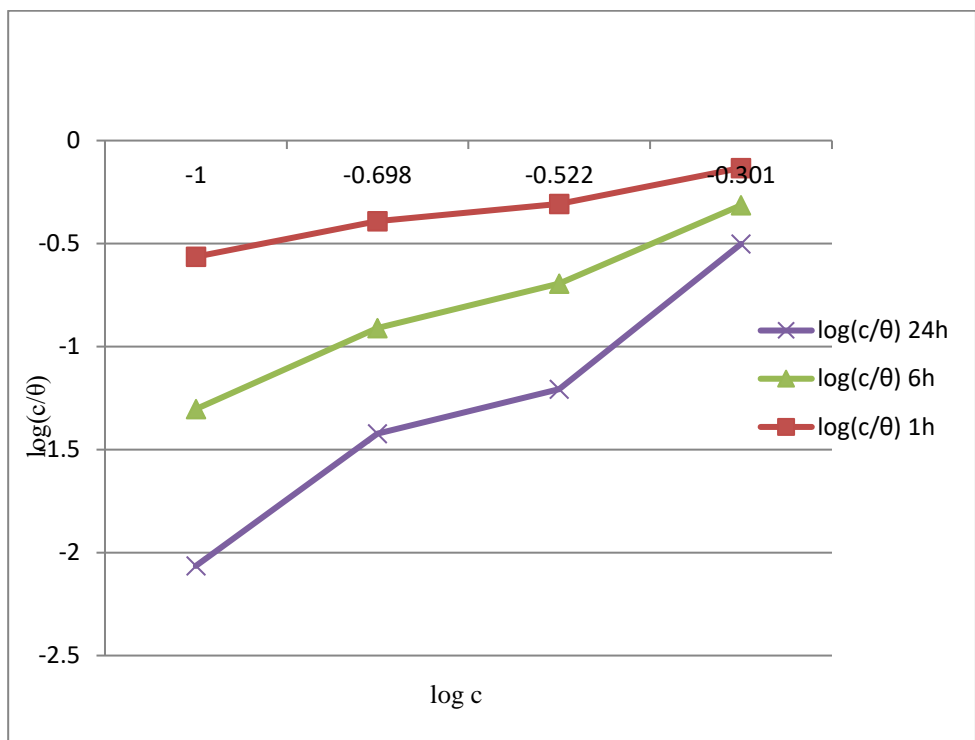


Figure: VIII: - Variation of $\log(c/\theta)$ with $\log c$ for Schiff's bases inhibitors for mild steel in 2.0N H₂SO₄ at 298+ 0.1K, Time at 1h,6h,24h, Area of exposure - 7.75cm²

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