International Journal of Scientific Research in Science and Technology
Available online at : www.ijsrst.com
OPEN ACCESS
Print ISSN: 2395-6011 | Online ISSN: 2395-602X
doi : https://doi.org/10.32628/IJSRST25121158

Electrochemical and Adsorption Studies Of Gymnema Sylvestre Leaves Extract on Mild Steel in 1.0 N Hydrochloric Acid

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ARTICLEINFO

Article History:

Accepted : 07 Jan 2025
Published: 09 Jan 2025

Publication Issue :
Volume 12, Issue 1
January-February-2025

Page Number :
67-72

ABSTRACT

In this article Gymnema sylvestre leaves extract have been taken for mild steel in 1.0N HCl was taken the adsorption studies and electrochemical studies were taken. The result approved in the conclusion area

I. INTRODUCTION

Corrosion is defined as the destruction of metals due to chemical or electrochemical reactions with the environment. It takes place because the metal should go back to their original stablest form viz., ores. It has been estimated that the cost of corrosion in worldwide
$2.2 trillion (6% GNP) [1] and in our country could be losing around Rs 2 lakh crore [2] every year owing to corrosion in various sectors including infra structure, utility services, production, manufacturing, defence and nuclear waste etc, The cost of corrosion has been found to raise every year.

II. BACKGROUNDOFTHE STUDY

Corrosion is often referred to as metallic deterioration by chemical attack or reaction of a metalwithitsenvironment.Itisaneverpresentandunceasingproblem,oftenhardtoeradicate totally. Deterrence would be more realistic and attainable rather than absolute elimination. Metallic deterioration progresses very fast after the destruction or penetration of the passive barrier which is followed by a number of reactions that alter the constituents and behaviour of both the superficial metal surface and the immediate environment. This is observed in, for example, oxides formation, and metal cation diffusion into the coating matrix, local pH changes, and electrochemical potential. The investigation of metallic corrosion is a subject of immense conceptual and practical concern and has thus received a substantial amount of interest. In industrial acid cleaning, pickling, descaling and oil well acidizing operations, acid solutions are widely employed on metal substrates to achieve the intended purpose. These processes however, require the use of corrosion inhibitors in order to reduce acid damage on metallic materials
In the chemical, oil, gas, automobile and transportation industries metallic degradation isoneofthemainfactorsinfluencingthedependabilityofthesystems.Forinstanceinoil,gas and petrochemical concerns thousands of kilometres of pipeline, pumps, pressure and storage vessels are used to process, store and transport products. These infrastructures are not only critical to the survival of these industries but also indirectly to the economy of the nation. However, because a large majority of these installations with their components are made of carbon steel andaluminium alloys theyareinevitablysusceptible to corrosionordegradation. In most cases these failures may result in product spillage which is invariably harmful to society as it represents a risk on safety, hazard to the environment and substantial loss of production time and money. It is also bad publicity for such concerns as compensation and litigation may be involved. For these reasons a lot of attention is paid to monitoring and inspection of these facilities. However, the period or duration at which these components are inspected can be prolonged or eliminated by incorporating sound corrosion protection techniques. Moreover, these techniques will reduce corrosion rate and by extension prolong inspection or monitoring time thereby reducing cost of operation.

III.STATEMENTOFTHE PROBLEM

Brass, Copper and mild steel are the major item of construction of the cisterns in the petrochemical industrial processes involving storage of acids (often referred to as hold up tanks) before use. This is a major operation in all industries utilizing these acids. The mild steel option as a material of choice is because

it is cheap and easily obtained when compared to stainless steel (six times as expensive). Also, in the transport of these acids from one point to another in the process plant, mild steel pipings are used because of the cost advantage. These pipings are also connected to fittings (valves, actuators and strainers) made of aluminium alloys and some other metallic alloys in some instances. However, they are prone to the damaging effects of the acid over time as they continuously interact with theacids. The damaging effects become obvious when the load carrying capacity of such facilities like shafts or shell thickness become compromised by reduction in the effective diameter or thickness as are sultofmetallos from corrosive attack. The effective diameter or thicknessis unabletosupportthetensile,compressiveorradialloadan dsofailurebecomes imminentand sometimes catastrophic.

IV. FREE ENERGY OF ADSORPTION:

The standard free energy of adsorption(ΔGads)can be calculated using the Equation and the observed negative values are (Table-1) ensure that the spontaneity of the adsorption process and the stability of the adsorbed layer is enhanced(ΔGads<-40Kj/mol). The value of ΔGads is less than -40 Kj/mol is commonly interpreted with the presence of physical adsorption by the formation of an adsorptive film with an electrostatic character. Therefore the adsorption of GSL inhibitor on mild steel surface is spontaneous and supports the mechanism of physical adsorption

TABLE1: CALCULATED VALUES OF ACTIVATION ENERGY (EA) AND HEAT OF ADSORPTION (QADS) OF GSL EXTRACT ON MILD STEEL IN 1.0N HCL ENVIRONMENT.

S.No	Conc. Of inhibitor (ppm)	% of I.E		Ea ($KJmol^{-1}$)	Q ads ($KJmol^{-1}$)
		30^o	60^o		
1.	0	-	-	14.6044	--
2.	10	20.00	27.11	11.9995	-11.1054
3.	50	42.85	32.20	19.3856	-12.7745
4.	100	57.14	42.37	22.8862	-16.6450
5.	500	71.42	47.45	31.6426	-28.4721
6.	1000	85.71	59.32	43.8702	-39.5588

3.1. ACTIVATION ENERGY

The values of corrosion rate obtained from the weight loss measurements were substitutedinequation-4.7andthevalueofactivationenergy(Ea)arepresentedinTable-6.4.Thevalueofactivation energyin theranges(14.6044–43.8702kJ/mol) formildsteel in1.0NHClcontaining various concentration ofinhibitor. Thevalueofactivation energy for blank (14.6044kJ/mol) islower than in thepresenceofinhibitors (Table-6.4) which is clearly indicates and suggests that the process is physisorption.

3.2. HEATOFADSORPTION

The values of heat of adsorption (Qads) on mild steel in hydrochloric acid containing various concentration of GSL extract was calculated using equation- 4.8. The Qadsvalues are ranged from -11.1054 to -39.588 kJ/mol (Table-1). These negativevalues are reflected that the adsorption of GSL extract on mild steel metal follows exothermic process.

3.3. THERMODYNAMICSPARAMETERS

Theanotherformoftransitionstateequationwhichisderivedfrom Arrheniusequation(4)is shown below

$CR=RT/Nhexp(\Delta S/R)exp(-\Delta H/RT)$

WherehisthePlanck'sconstant,NtheAvogadro'snumber , ΔStheentropyofactivation,and ΔH the enthalpy of activation .A plot of log(CR/T)Vs.1000/Tgives a straight line(Fig.1)with a slope of(–ΔH/R)and an intercepttof[log(R/Nh))+(ΔS/R)],from which the values of ΔS and ΔH were Calculated and listed in Table 1 .The positivevalue of enthalpy of activationclearthat the endothermic nature of dissolution process is very difficult. The entropy(ΔS) is generally interpreted with disorder which may take place on going from reactants to the activated complex.

TABLE 2: THERMODYNAMIC PARAMETERS OF MILD STEEL IN 1.0N HCl OBTAINED FROM WEIGHT LOSS MEASUREMENTS.

S.No	Concentration of GSL(ppm)	ΔH (kJmol–1)	ΔS (Jk–1mol–1)
1	0	4.7115	8.6462
2	10	3.3270	8.1252
3	50	6.3067	9.0022
4	100	7.5829	9.3355
5	500	11.0769	10.3627
6	1000	15.5875	11.6537

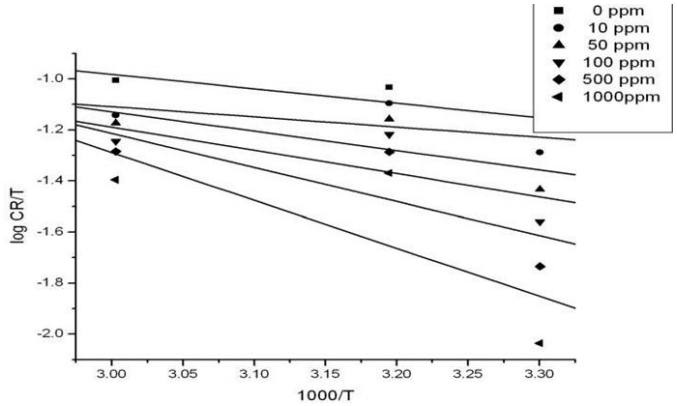

FIGURE-1: THE RELATION BETWEEN LOG (CR/T) AND 1000/T FOR DIFFERENT CONCENTRATIONS OF GSL EXTRACT ELECTROCHEMICAL STUDIES POTENTIODYNAMIC POLARIZATION MEASUREMENTS

The potentiodynamic polarization measurement of mild steel in 1.0 Nhydrochloric acid containing different concentration of Gymnema Sylvestre leaves extract was studied and the observed data are placed in Table-(Fig-3). It was found out that the corrosion current density (Icorr) decreased from 82.92to1.65μA/cm2 with increase of inhibitor concentration. The Corrosion potential (Ecorr) was shifted to negative direction from 215to322mV clearly indicates that an adherent film formed on the metal surfaceof mild steel in acid media. The inhibitor was mixed type and it was effective in controlling both anodic and cathodic dissolution of mild steel in acid environment. The inhibition efficiency attained maximum of 98.04% at 1000ppm concentration. Also this green inhibitor is more excellent for mild steel in acid environment

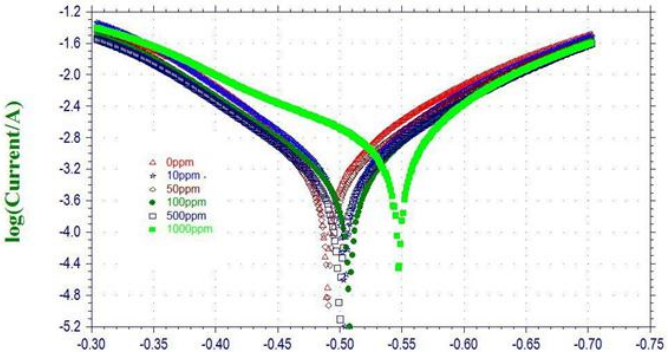

FIG-2:TAFELPLOTOFMILDSTEELIN1 N HCL CONTAINING VARIOUS CONC. (0 TO 1000 PPM) OF GSL EXTRACT

The observed data suggests that there was a good correlation between the percentage of inhibition efficiencies calculated from weight loss data.

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) MEASUREMENTS

Electrochemical impedance technique is a powerfultool intheinvestigation ofthe corrosion and adsorption phenomena. Fig-3(a) shows that smooth semicircle of a Nyquistplotformildsteelin1.0Nhydrochloricacidcontaining variousconcentrationsof leavesextract.Table-3 reflects that the charge transfer resistance(Rct)values increased from16.35to 360.12Ωcm-2 with increase of inhibito rconcentration in acid environment. and attained maximum of 93.5% inhibition efficiency. The higher value of Rctwas attributed to the stable passive layer formed at the inhibitor-electrode interface and the effective behaviour of the inhibitor coating,which limits diffusion of the corrosivespecies towards the mild steel surface. The decrease of double layer capacitance (Cdl) values showed that the adsorption of active molecules on the metal surface leading to a thin film formation. Also these results are in good agreement with the previous results.

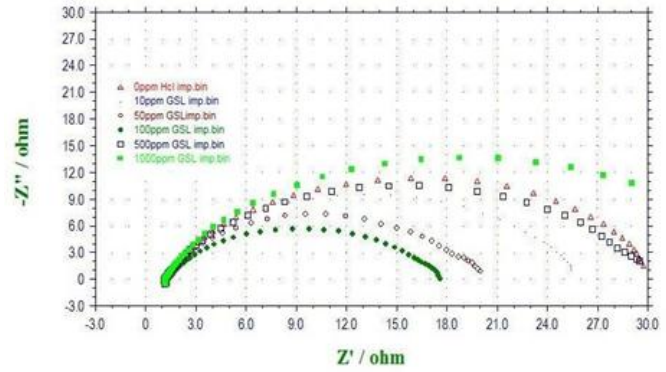

FIG-3(a): ELECTROCHEMICAL IMPEDANCE PLOTS OF MILD STEEL IN 1.0 N HCL CONTAININGVARIOUSCONC.(0TO1000PPM)OF GSL EXTRACT

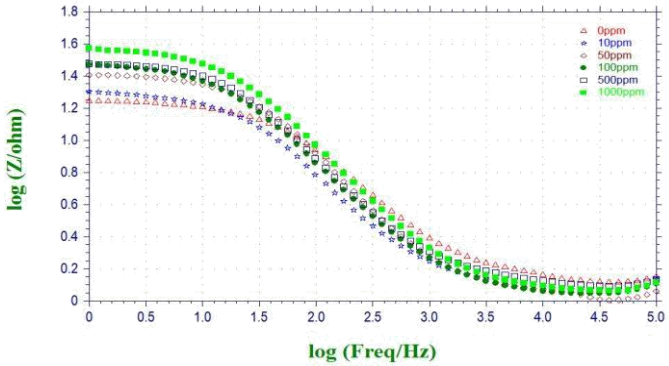

FIG-3(b): BODE ANGLE PLOT OF MILD STEEL IN 1N HCL CONTAINING VARIOUSCONC. (0TO1000PPM) OFGSLEXTRACT

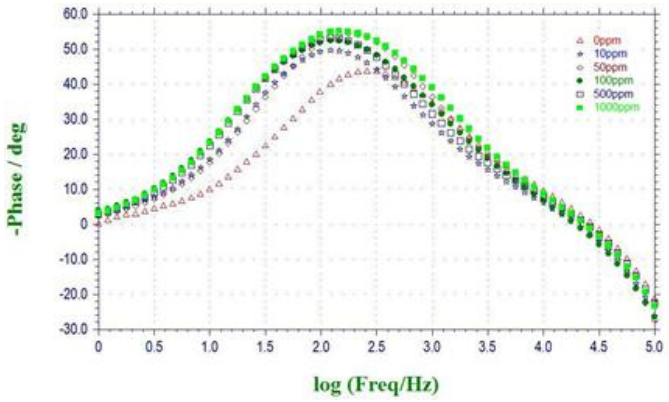

FIG-3(c): PHASE ANGLE PLOT OF MILD STEELIN1NHCLCONTAININGVARIOUS CONC. (0TO1000PPM)OF GSL EXTRACT

TABLE3: PARAMETERS DERIVED FROM ELECTROCHEMICAL MEASUREMENTS OF MILD STEEL IN 1.0 N HCL CONTAINING VARIOUS CONC. (0 TO 000PPM) OF GSL EXTRACT

Conc. (ppm)	Polarisationstudies					Impedancestudies		
	-E_{corr}(mV vs SCE)	b_a(mV/ decade)	b_c(mV/ decade)	I_{corr}(A/cm^2)	I.E (%)	R_{ct}	C_{dl}(µF/cm^2)	I.E (%)
Blank	215	106	204	148.6	---	16.353	0.0009717	---
10	244	107	163	69.01	16.77	19.027	0.0007347	13.18
50	266	110.37	92.86	56.29	32.11	24.84	0.0004909	17.91
100	283	106.36	95.83	52.42	36.80	28.068	0.0003912	46.9
500	294	94.51	109.47	48.10	70.21	72.58	0.000035	70.2
1000	322	16.05	123.47	1.65	98.04	360.12	0.0000014	93.5

V. CONCLUSION

Inhibition effect of Gymnema Sylvestre leaves(GSL)extractonMildsteelin1.0N hydrochloric acid was studied by both electrochemical and non-electrochemical methods.

The thermodynamic parameters namely; activation energy (Ea), heat of adsorption (Qads) and free energy of adsorption (ΔGads) values describes the adsorption of inhibitor on the metal surface is physisorption ,endothermic and spontaneous process.

The inhibitor obeys Langmuir adsorption isotherm.Since the average regression coefficient value(R2 = 0.9924) is almost close to unity

In potentiodynamic polarization measurement the values of corrosioncurrent density (Icorr) decreased from 82.92 to 1.65 µA/cm2 with increase of inhibitor concentration and attained maximum of 98.04% at 1000 ppm. The inhibitor is mixed type inhibitor.

In electrochemical impedancespectroscopy(EIS)measurements,thevalueof Charge transfer resistance(Rct) increased from16.35to360.2Ωcm-2and thedoublelayercapacitance(Cdl)values decreased from 97.17 to 14.08 µFcm-2 with increase of inhibitor concentration and attained maximum of 93.5%at 1000ppm suggests that the protective film prevent further dissolution of inhibitor molecules

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