Electrochemical and adsorption studies of cardiospermum halicababum leaves extract in 0.1N Hydrochloric acid

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***Abstract*—In this article cardiospermum leaves extract have been taken for brass in 0.1N HCl was taken the adsorption studies and electrochemical studies were taken. The result approved in the conclusion area**

***Index Terms*—About four(minimum) key words or phrases in alphabetical order, separated by commas.**

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, defense 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 metal with its environment. It is an ever present and unceasing problem, often hard to eradicate 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 behavior 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 is one of the main factors influencing the dependability of the systems. For instance, in oil, gas and petrochemical concerns thousands of kilometers 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 and aluminum alloys they are in evitable susceptible to corrosion or degradation. 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 aluminum 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 the acids. Thedamaging 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 s from corrosive tack. The effective diameter or thickness is unable to support the tensile, compressive or radial load and so failure becomes imminent and sometimes catastrophic.

IV. EFFECT OF TEMPERATURE ADSORPTION STUDIES

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and it characteristic of inhibitor on the metal surface. In our present study an attempt of Langmuir adsorption isotherm, Temkin, frendlich, frumkin, Elawady adsorption isotherm are investigated. The straight lines observed in Fig- 5.1 suggest that the inhibitor follows Langmuir adsorption isotherm which suggests that there was no interaction between the adsorbed species. Langmuir adsorption isotherm model is more suitable to represent the corrosion rate data than Frumkin, Temkin, Florry Huggins adsorption isotherm model, and the regression values (R^2) of Langmuir adsorption isotherm model approach unity with average value of about (0.9946), while the average values of R^2 obtained from Frumkin (0.9818), Temkin(0.96929) Frendlich (0.9804) Florry Huggins(0.93126) and El awady (0.98165). The Values relatively far from unity as compared with the values obtained from Langmuir adsorption isotherm.

Table-5.3. Various Adsorption Parameters for TheAdsorption Of Chl Inhibitor On Brass In 1.0 N Hcl Environment

ADSORPTION ISOTHERM	TEMPERATURE (K)	LOG K	SLOPE	R^2	ΔGads
Langmuir	303	0.7326	7.8058	0.9969	-15.2971
	313	0.7013	22.4124	0.9908	-18.5471
	333	0.7110	12.3370	0.9961	-18.0791
Temkin	313	-0.10172	0.29315	0.97507	-10.389
	323	-0.05768	0.12854	0.95339	-10.430
	333	-0.08589	0.21437	0.97941	-10.573
Frendlich	313	-0.89122	0.2762	0.98838	-5.112
	323	-1.35113	0.2914	0.97534	-2.4313
	333	-1.0918	0.28896	0.9884	-4.623
Frumkin	313	-0.53956	5.2302	0.98985	-6.895
	323	-0.51759	9.52345	0.96897	-7.585
	333	-0.54427	6.50575	0.98675	-7.6513
	313	-1.65641	2.09746	0.92659	-5.256

Florry Huggins	323	-1.9331	8.30085	0.91543	-1.1689
	333	-1.68456	4.24731	0.95175	-3.7082
El-Awady	313	-0.97886	0.16776	0.98829	-4.5850
	323	-1.14476	0.19872	0.9845	-3.705
	333	-1.37756	0.22814	0.97216	-2.338

The Value of activation energy (Ea) for the corrosion of Brass in the presence and absence of CHL extract in 1.0N Hydrochloric acid is determined utilizing the Arrhenius equation-4.6 and its inferred frame equation-4.7. The estimation of activation energy ranges from - 9.4104 to 13.4153 kJ/mol for Brass in 1. ON Hydrochloric acid containing different concentration of inhibitor. The average value of Ea acquired from the clear (- 9.4104 kJ/mol) is lower than within the sight of inhibitor and suggest that there is a physical adsorption between the CHL inhibitor atom and the metal of Brass surface.

Table-5.4: Calculated Values Of Activation Energy (Ea)And Heat Of Adsorption (Qads) Of Chl Extract On Brass In 1.0 N Hcl Environment

S. No	Conc. of inhibitor(ppm)	% of I. E		Ea($KJmol^{-1}$)	Q ads ($KJmol^{-1}$)
		30º	60º		
1.	0	-	-	-9.4104	--
2.	10	25.00	14.99	-5.9097	-17.8058
3.	50	32.14	24.99	-6.6110	-9.8360
4.	100	46.42	34.99	-4.0021	-13.3115
5.	500	67.85	44.99	5.6127	-26.5072
6.	1000	82.14	60.00	13.1453	-31.3357

A. Heat of Adsorption

The heat of adsorption on Brass in the existence of inhibitor in acid medium is calculated from the equation- 4.8. The Qads values are ranged from -17.8058 to -31.3357 kJ/mol (Table- 5.3) and clearly indicates that the adsorption of CHL extract on the surface of Brass metal is exothermic process

B. Thermodynamics Parameters

Another form of transition state equation which is derived from Arrhenius equation isshown below

CR=RT/Nh exp (ΔS/R) exp (-ΔH/RT)

Where h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation. A plot of log (CR/T) Vs. 1000/T gives a straight line (Fig. 5.3) with a slope of (−ΔH/R) and an intercept of [log(R/Nh)) + (ΔS/R)], from which the values of ΔS and ΔH were calculated and listed in Table-5.3. The negative value of enthalpy of activation clear that 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 1: Thermodynamic Parameters of Brass In 1.0nHcl Obtained from Weight Loss Measurements.

S. No	Concentration of CHL (ppm)	ΔH ($kJ\ mol^{-1}$)	ΔS ($J\ k^{-1}mol^{-1}$)
1	0	-7.3246	46.8965
2	10	-6.1675	49.9165
3	50	-6.5141	48.4376
4	100	-5.7540	50.3403
5	500	-2.3289	60.2940
6	1000	0.2440	67.1248

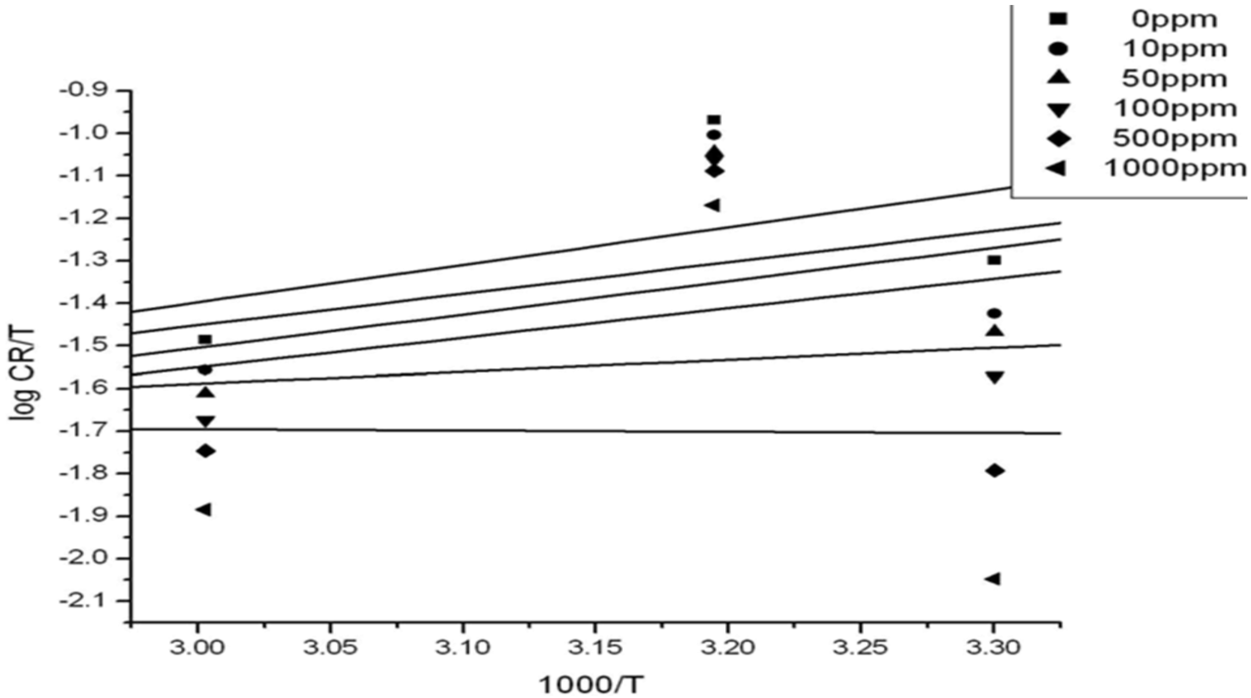


Figure-1 The Relation Between Log (Cr/T) And 1000/T forDifferent Concentrations of Chl Extract

V. ELECTROCHEMICAL STUDIES

A. Potentiodynamic Polarization Measurements

Table-5.6 reflects that the various parameters of potentiodynamic polarization studies of Brass in 0.1 N hydrochloric acid with and without addition of different concentrations of *Cardiospermum halicababum* leaves extract (Fig-1). The corrosion current density (Icorr) values decreased with increase of inhibitor concentration. Corrosion current more significantly reduced from 322.6 to 2.65 µA/cm^2 can be due to the adsorption of inhibitor molecules on the metal surface almost completely covered. The value of corrosion potential (Ecorr) was shifted to negative direction i.e., from 204 to 294 mV.

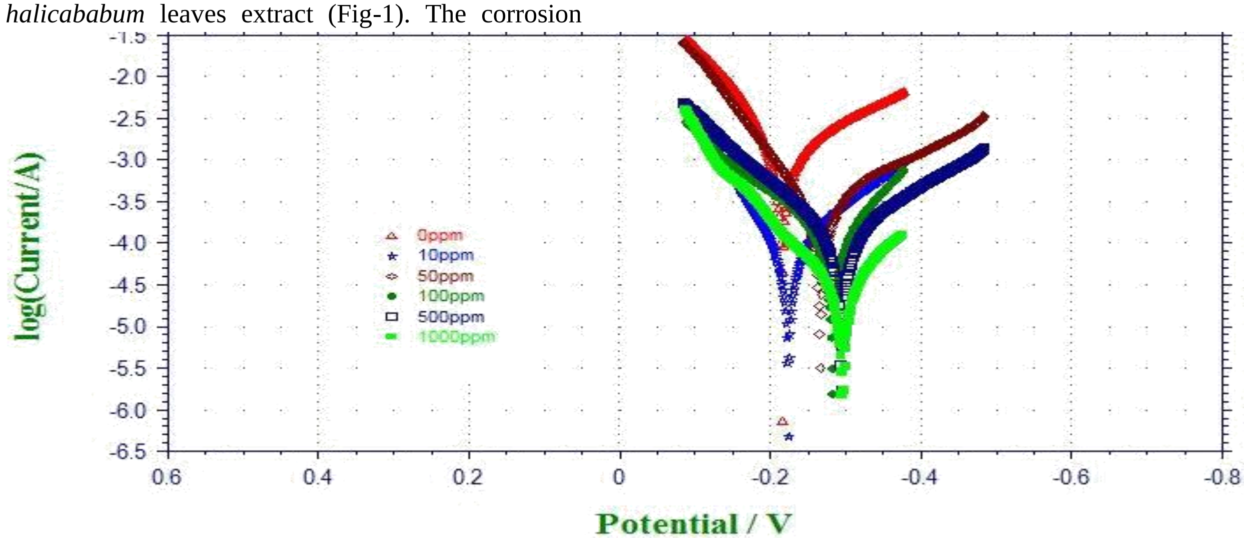


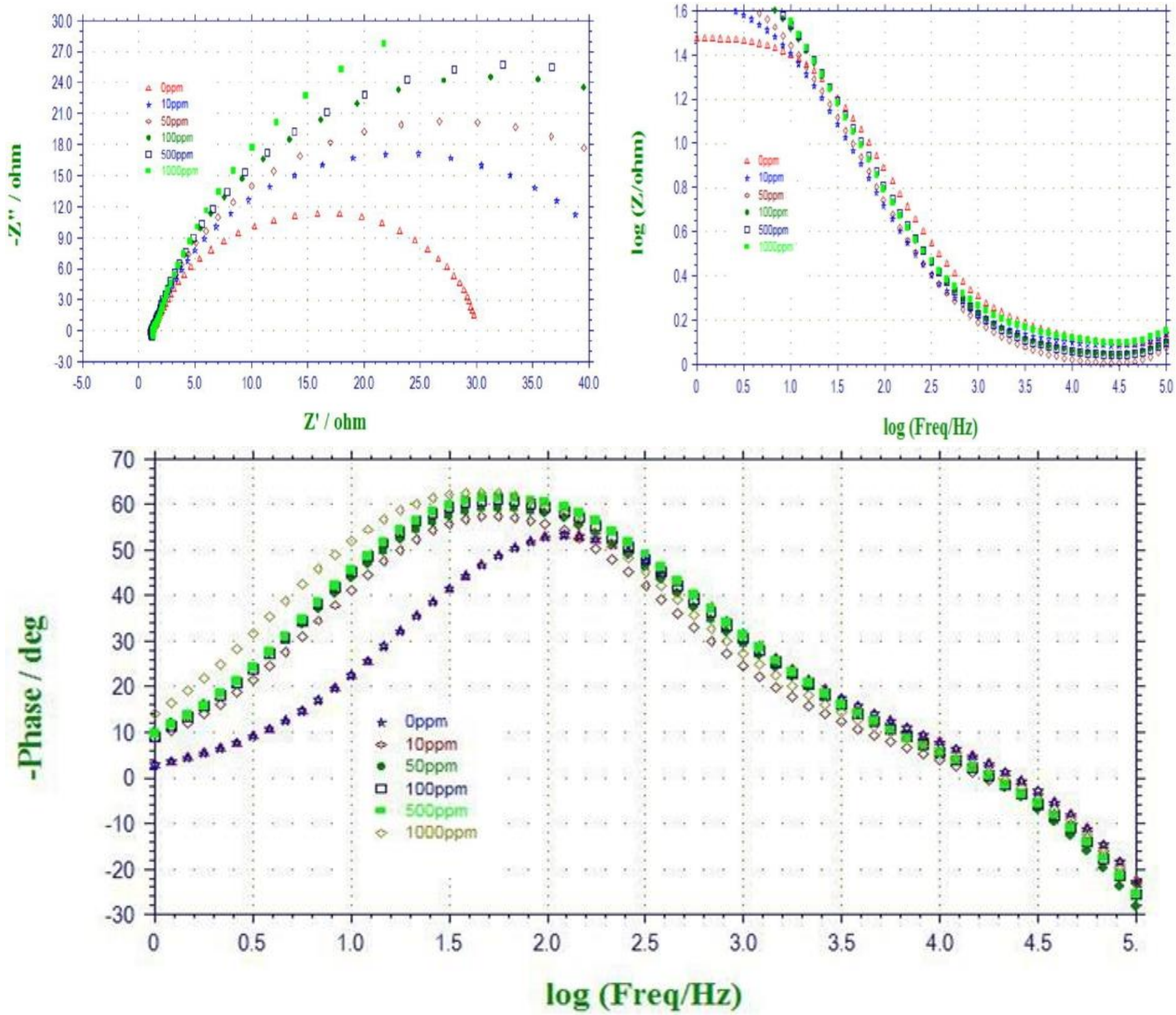
Fig-2: Tafel Plot of Brass In 1.0 N Hcl Containing Various Conc. (0 To 1000 Ppm) Of Chl Extract

The percentage of inhibition efficiency of *Cardiospermum halicababum* leaves extract attained a maximum value of 96.04% at 1000 ppm of inhibitor concentration. This result also in very good agreement with those observed from the previous data. The values of inhibition efficiency increased with increase of inhibitor concentration, clearly suggests that a maximum surface coverage was obtained with optimum concentration of inhibitor. The effectof the anodic polarization behavior of Brass (Fig-5.3) suggests that the protective thin films formed on the metal surface can alter anodic dissolution in solution shows that *Cardiospermum halicababum* leaves extract formed a thin film that acted as a barrier to protect the metal surface from corrosion environments. Also, the inhibitor is anodic type.

VI. ELECTROCHEMICAL IMPEDANC ESPECTROSCOPY (EIS)

A. Measurements

The electrochemical impedance spectroscopy (EIS) measurements for Brass in 1.0 N hydrochloric acid containing various concentrations of CHL leaves extract and the parameters are shown in Table-5.6. The semicircle of the nyquists plots (fig (2) shows that size of the loop increased with increase of inhibitor concentration and the shape is maintainedthroughout the experiment.



1(a)Fig-1(a-c): Electrochemical Impedance plots, (a) Nyquist plot (b) Bode plot c) Phase angle plot for Brass in 1.0 plot for Brass in 1.0 N HCl containing various conc. (0 to 1000 ppm) of CHL extract onBrass

Charge transfer resistance (Rct) values are increased from 28.52 to 80.02 Ω cm^{-2} and double layer capacitance (Cdl) values are decreased from 87 to 11 µF cm^{-2} with increase of inhibitor concentration. The percentage of inhibition efficiency attained maximum of 94.5%at 1000ppm of inhibitor concentration. The moderate increase of Rct values confirm that the protective layer formed on the metal surface and corrosion of Brass is controlled maximum in the presence of inhibitor.

In Fig-5.4(b-c) shows that the Bode and Phase angle plots for Brass in 1.0 N hydrochloricacid containing various concentration of *Cardiospermum halicababum* leaves extract. The Bode plot and its phase angle increased with rise in inhibitor concentration and suggest that the dissolution rate decreased with increase of inhibitor concentration. The observed results EIS, also very good agreement with the previous agreement

Table-5.6: Parameters Derived from Electrochemical Measurements Of Brass In 1.0 N Hcl Containing Various Conc. (0 To 1000 Ppm) Of Chl Extract

Conc. (ppm)	Polarisation studies					Impedance studies		
	-Ecorr (mV vs SCE)	ba (mV/ decade)	bc (mV/decade)	Icorr (A/cm^2)	I.E (%)	Rct (Ω)	Cdl ($\mu F/cm^2$)	I.E (%)
Blank	204	106.64	213.73	322.6	---	28.52	0.0008717	---
10	215	107.33	163.19	286.01	16.77	42.05	0.0007547	15.18
50	244	92.19	241	206.29	32.11	49.40	0.0006309	29.91
100	266	86.36	172.83	180.42	36.80	57.55	0.0004012	52.9
500	283	136.51	172.68	48.10	70.21	69.5	0.000020	70.2
1000	294	15.05	80.47	2.65	96.04	80.2	0.0000014	94.5

VII. CONCLUSION

- Using Cardiospermum halicabaum leaves the above observations the following conclusions were drawn:
- The inhibition effect of *Cardiospermum Halicababum* leaves (CHL) extract on Brass in 1.0 N hydrochloric acid was studied by both electrochemical and non- electrochemical methods.
- In Weight loss studies in the presence of CHL inhibitor, the value of corrosion rate was moderately decreased with increase of inhibitor concentration and
- attained maximum of 91.67 % of inhibition efficiency was achieved at 1000 ppmof inhibitor concentration.
- In temperature studies, in the presence of CHL extract the value of corrosion rate was reduced from 15.2083 to 2.7157 mmpy at 313 K and maximum of 82.14%
- inhibition efficiency was attained at 313 K.
- Thermodynamic parameters viz; activation energy (Ea), heat of adsorption (Qads)and free energy of adsorption (Gads) values suggests that the adsorption of inhibitor on the metal surface is physisorption, exothermic and spontaneous process.
- The inhibitor obeys both Langmuir adsorption isotherm. Since the averageregression value(R^2) very close to unity (0.9946)
- In potentiodynamic polarization studies, the values of corrosion current density
- (Icorr) decreased with increase of inhibitor concentration 322.6 to2.65 µA/cm^2 andattained a maximum of 98.04% inhibition efficiency at 1000 ppm
- In electrochemical impedance spectroscopy (EIS) measurements, the value of Charge transfer resistance (Rct) increased from 28.52 to 80.2 Ωcm^{-2} and the
- double layer capacitance (Cdl) values decreased from 87.17 to 1.4 µFcm^{-2} with increase of inhibitor concentration and attained maximum of 94.5%

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