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Ultrasound Assisted Synthesis of Chalcones as Green Corrosion Inhibitors for Mild Steel in 1M Hydrochloric Solution

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The three chalcones namely (E)-3-(4-hydroxyphenyl)-N-phenylacrylamide (INH-1), (E)-3-(4dimethylamino)phenyl)-N-phenylacrylamide (INH-2) and (E) -3-(4-hydroxy-3-methoxyphenyl)-N-phenylacrylamide (INH-3) were synthesized and their corrosion inhibition properties on mild steel in 1M HCl was investigated using weight loss, potentiodynamic polarization method, linear polarization resistance (*LPR*) and electrochemical impedance spectroscopy (*EIS*) techniques. Potentiodynamic results showed that, chalcones are act as mixed type inhibitors and adsorption of these compounds follow Langmuir adsorption isotherm. Nyquist plots indicates that the addition of chalcones increases the charge-transfer resistance (R_{ct}) and decreases the double-layer capacitance (C_{dl}) of the corrosion process this reveals that investigated chalcones inhibits mild steel corrosion by adsorption on its surface. Some thermodynamic and kinetic parameters also determined in relevance to describe the mechanism of adsorption.

Keywords: *Chalcone, Acid corrosion, mild steel, thermodynamic parameters, EIS*

1. INTRODUCTION

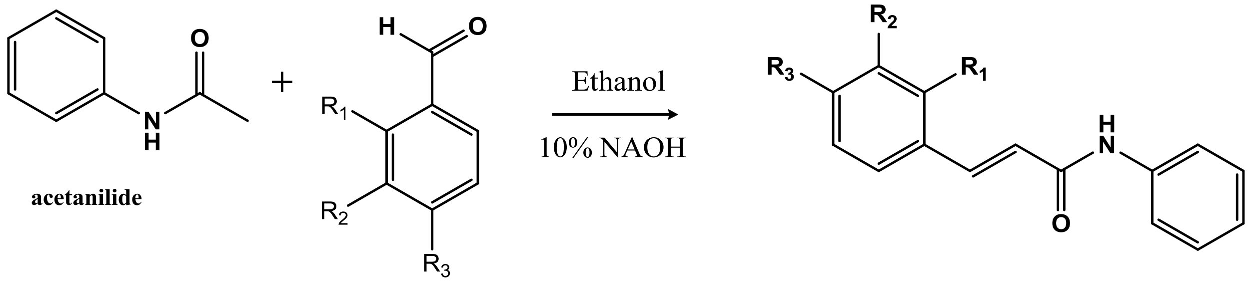
The use of inhibitors to control the destructive attack of acid environment has found widespread applications in many industrial processes such as acid cleaning, acid pickling, acid descaling, and oil well acidizing [1]. The mild steel has a wide application in various industries as construction material for chemical reactors, heat exchange and boiler systems, storage tanks, and oil and gas transport pipelines due to its high mechanical properties and low cost [2]. Organic compounds containing polar functions with oxygen, nitrogen, or sulfur have been widely studied as inhibitors for the acid corrosion of steel. These substances generally become effective by adsorption on metal surface. The efficient adsorption is the result of either the π-electron of the aromatic system and multiple bonds, or the presence of electronegative atoms (O or N) in the inhibitors molecular structure [3]. Availability of *π* electron due to the presence of multiple bonds or aromatic rings in the inhibitors molecule would facilitate electron interact with d-orbital of iron [4-5]. Chalcones of are great importance in different field for example medicinal chemistry, antibacterial, antifungal, insecticidal, anesthetic, anti inflammatory, analgesic etc [6-11] . In the view of the various chemical and biological applications, few chalcones have recently been reported as effective corrosion inhibitors for mild steel [12-18]

The aim of this paper is to study the inhibiting action of three synthesized chalcones of acetanilide and aldehydes containing nitrogen, oxygen and aromatic rings. The study was conducted by weight-loss, potentiodynamic polarization, linear polarization resistance (*LPR*) and electrochemical impedance spectroscopy (*EIS*). Several isotherms were also tested for their relevance to describe the adsorption behavior of investigated chalcones. To study the effect of temperature on the corrosion behavior of mild steel weight-loss experiment carried at different temperature in the absence and presence of optimum concentration of chalcones.

2. EXPERIMENTAL

2.1 Inhibitors synthesis

Chalcones were synthesized according to the scheme 1 as describe earlier in literature [19]. The chalcones were by gradual addition of base (NaOH) in alcoholic solution of acetanilide and aldehydes. The reaction mixture was stirred for 6 hours. The synthesis was also achieved by ultrasonication of above reaction mixture for 20-25 min in ethanol. The purity of the product was confirmed by thin-layer chromatography in ethyl acetate/n-hexane (4:6) as developing solvent using the Silica Plate (TLC Plates−Aluminum (Al) Silica.



Scheme 1. Synthetic scheme of chalcones

INH-1, R_1= -OH, R_2= -H, R_3= -H **INH-2**, R_1= -H, R_2= -H, R_3= -N $(CH_3)_2$
INH-3, R_1= -H, R_2= -OH, R_3= $-OCH_3$

2.2. Materials

The mild steel specimens, with composition (wt %) Fe 99.30%, C 0.076%, Si 0.026%, Mn 0.192%, P 0.012%, Cr 0.050%, Ni 0.050%, Al 0.023%, and Cu 0.135%, was abraded successively with emery papers from 600 to 1200 mesh/in grade, washed with double distilled water, degreased with acetone and finally dried in hot air blower. The working electrode (WE) was a 7.0 cm long stem (isolated with epoxy resin) to provide an exposed surface area of 1.0 cm^2 for electrochemical measurements and dimension 2.5 × 2.0 × 0.025 cm^3 were used in weight loss measurements. The test solution 1 M HCl prepared from analytical reagent grade reagent (37 % HCl) and double distilled water.

2.3. Weight loss method

The weight loss measurements were carried out by standard method as described earlier [20].The inhibition efficiency (η%) and surface coverage (θ) were calculated by using the following equations:

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \qquad (1)$$

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \qquad (2)$$

where C_R and $C_{R(i)}$ are the corrosion rate values in absence and presence of chalcones respectively. The corrosion rate (C_R) of mild steel in acidic medium was calculated by using following equation:

$$C_R = \frac{W}{At} \qquad (3)$$

where , W is weight loss of mild steel specimens (mg), A is the area of the specimen (cm^2) and t is the exposure time (h).

2.4 Electrochemical measurements

The Potentiostat/Galvanostat having a Gamry framework system based on ESA 400 in a frequency range of 10^{-2} Hz to 10^5 Hz under Potentiodynamic conditions, with amplitude of 10 mV peak-to-peak, using AC signal at E_{corr} were used for electrochemical measurements. The Potentiostat/Galvanostat consists of three electrodes assembly, the mild steel (working electrode), saturated calomel (reference electrode) and platinum foil (counter electrode). Gamry applications include software DC105 for corrosion and EIS 300 and Echem Analyst version 5.50 software packages was used for data fitting. All electrochemical experiments were performed in aerated 1M HCl solution with and without chalcones. Prior to the electrochemical measurements the working electrode was immersed in 1 M HCl in absence and presence of chalcones for 30 minutes to stabilization of the *OCP w.r.t. SCE*. All the impendence measurements were performed under a potentiodynamic condition from 100,000 Hz to 0.01 Hz with amplitude of 10 mV peak-to-peak. The polarization measurements were performed by changing the electrode potential automatically from -250 to +250 mV vs. *OCP* at a scan rate of 1 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion current densities (I_{corr}). The linear polarization study was carried out from cathodic potential of −20 mV vs. *OCP* to an anodic potential of +20 mV vs. *OCP* at a scan rate 0.125m*V* s^{-1} to study the polarization resistance (R_p). The inhibitive efficiency was calculated by Equations (4) and (5) [21,22].

$$\eta\% = \left(1 - \frac{I_{corr(i)}}{I_{corr}}\right) \times 100 \qquad (4)$$

$$\eta\% = \left(1 - \frac{R_{ct}}{R_{ct(i)}}\right) \times 100 \qquad (5)$$

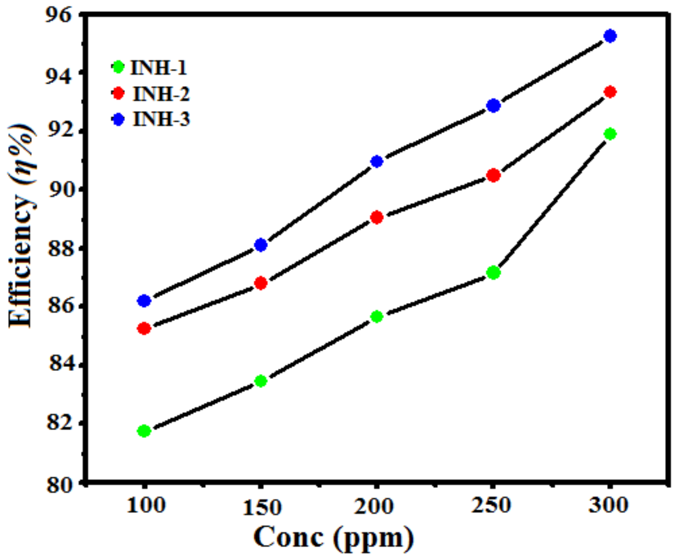
I_{corr} *and* $I_{corr(i)}$ signify the corrosion current density in the absence and presence of chalcones*;* $R_{ct(i)}$ and R_{ct} are charge transfer resistance in the presence and absence of the chalcones.

3. RESULTS AND DISCUSSION

3.1 Weight loss studies

3.1.1 Effect of inhibitor concentration

The values of percentage inhibition efficiency (η %) and corrosion rate (C_R) and corresponding surface coverage (θ) obtained from weight loss method at different concentrations of chalcones are summarized in Table 1. It has been found that inhibition efficiencies increase with increase in concentrations of chalcones.



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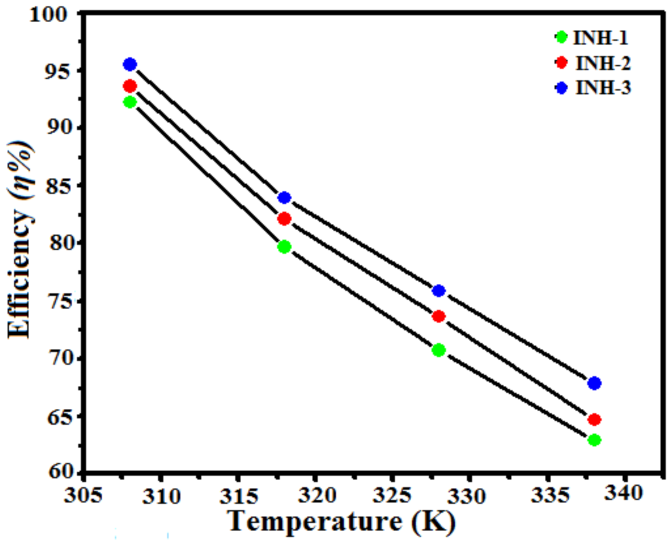

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Figure 1. (a) Inhibition efficiency of chalcones at different concentration (b) Inhibition efficiency of chalcones at different temperature

The maximum inhibition efficiency was obtained at 300 ppm and further increase in concentration did not cause any appreciable change in the inhibition performance of chalcones. The corrosion rate values decreases and inhibition efficiencies increase with the chalcones concentrations. The variation of inhibition efficiency with chalcones concentration is shown in Figure 1(a). From Table 1, it is clear that the order of the inhibition efficiency of Chalcones is as follows: INH-1 < INH-2 < INH-3. This order of inhibition efficiency can be explain on the basis of substituents present in aldehydic ring of chalcones. The higher inhibition efficiency of INH-2 over INH-1 is due to presence of more electron releasing –N $(CH_3)_2$ group as compared to –OH group of INH-1. The best inhibition efficiency of the INH-3 is due presence of two electron releasing (-OH, $-OCH_3$) groups.

3.1.2. Effect of temperature

Table 1. Corrosion rate (C_R), Surface coverage (θ) and corrosion inhibition ($\eta\%$) for mild steel in 1M HCl in absence and in presence of different concentrations of Chalcone from weight loss measurements at 308 K.

Inhibitor	Inhibitor conc ppm	Corrosion rate (mg cm^{-2} h^{-1})	Surface coverage (θ)	η%
Blank	0.0	7.0	……	….
INH-1	100	1.86	0.7689	76.89
	150	1.66	0.7893	78.93
	200	1.40	0.8000	80.00
	250	0.92	0.8714	87.14
	300	0.56	0.9190	91.90
INH-2	100	1.03	0.8523	85.23
	150	0.86	0.8761	87.61
	200	0.76	0.8904	89.04
	250	0.66	0.9047	90.47
	300	0.46	0.9333	93.33

INH-3	100	0.96	0.8619	86.19
	150	0.83	0.8809	88.09
	200	0.63	0.9095	90.95
	250	0.51	0.9285	92.85
	300	0.33	0.9523	95.23

The influence of solution temperature on inhibition efficiency was also investigated by performing the weight loss experiment at different temperature (308-338 K). The variation of inhibition efficiencies with temperature is shown in Figure 1(b). It is observed that inhibition efficiency decreases with increase in temperature. The decrease in inhibition efficiency with temperature may be attributed to desorption of the chalcones molecule from metal surface at higher temperature [23]. At elevated temperature, desorption of chalcones causes greater surface area of mild steel to comes in contact with acid solution, resulting in an increase in corrosion rate. These results confirm that chalcones are excellent corrosion inhibitors for mild steel in 1 M HCl at lower temperature and their inhibition efficiency decreases with increase in temperature.

3.2.3 Thermodynamic parameters and adsorption isotherm

The mechanism of corrosion inhibition may be explained on basis of adsorption behavior [24]. Several adsorption isotherms were tested to describe the adsorption behavior of all the Chalcone used in study, in which Langmuir adsorption isotherm shows best fit. A straight line was obtained on plotting log C vs $\log\theta/(1-\theta)$ for all the chalcone used in study shown in Figure 2 (a). The degree of surface coverage (θ) for different concentrations of all chalcones was evaluated from weight loss data. It is found that all the compounds under study obey Langmuir adsorption isotherms, which is given by following equation.

$$\frac{C_{(\mathrm{inh})}}{\theta} = \frac{1}{K_{(\mathrm{ads})}} + C_{(\mathrm{inh})} \qquad (6)$$

where K_{ads} is the equilibrium constant of the adsorption–desorption process, θ is the degree of surface coverage and C_{inh} is molar concentration of chalcones in the bulk solution. Though the Langmuir adsorption isotherm is linear [Figure 2 (a), correlation > 0.9], deviation of slope from unity (for ideal Langmuir isotherm) can be attributed to the molecular interaction among the adsorbed chalcones species, a factor which was not taken into consideration during the derivation of the Langmuir equation [25]. Langmuir isotherm assumes that:

(i) The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.

(ii) ΔG^{o}_{ads} is the same for all sites and it is independent of θ.

(iii) The adsorbates do not interact with one another, i.e. there is no effect of lateral interaction of the adsorbates on ΔG^{o}_{ads} [26].

It is well recognized that the first step in inhibition of metallic corrosion is the adsorption of organic inhibitors molecules at the metal/solution interface and that the adsorption depends on the molecule’s chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent H_2O molecules could also adsorb at metal/solution interface.

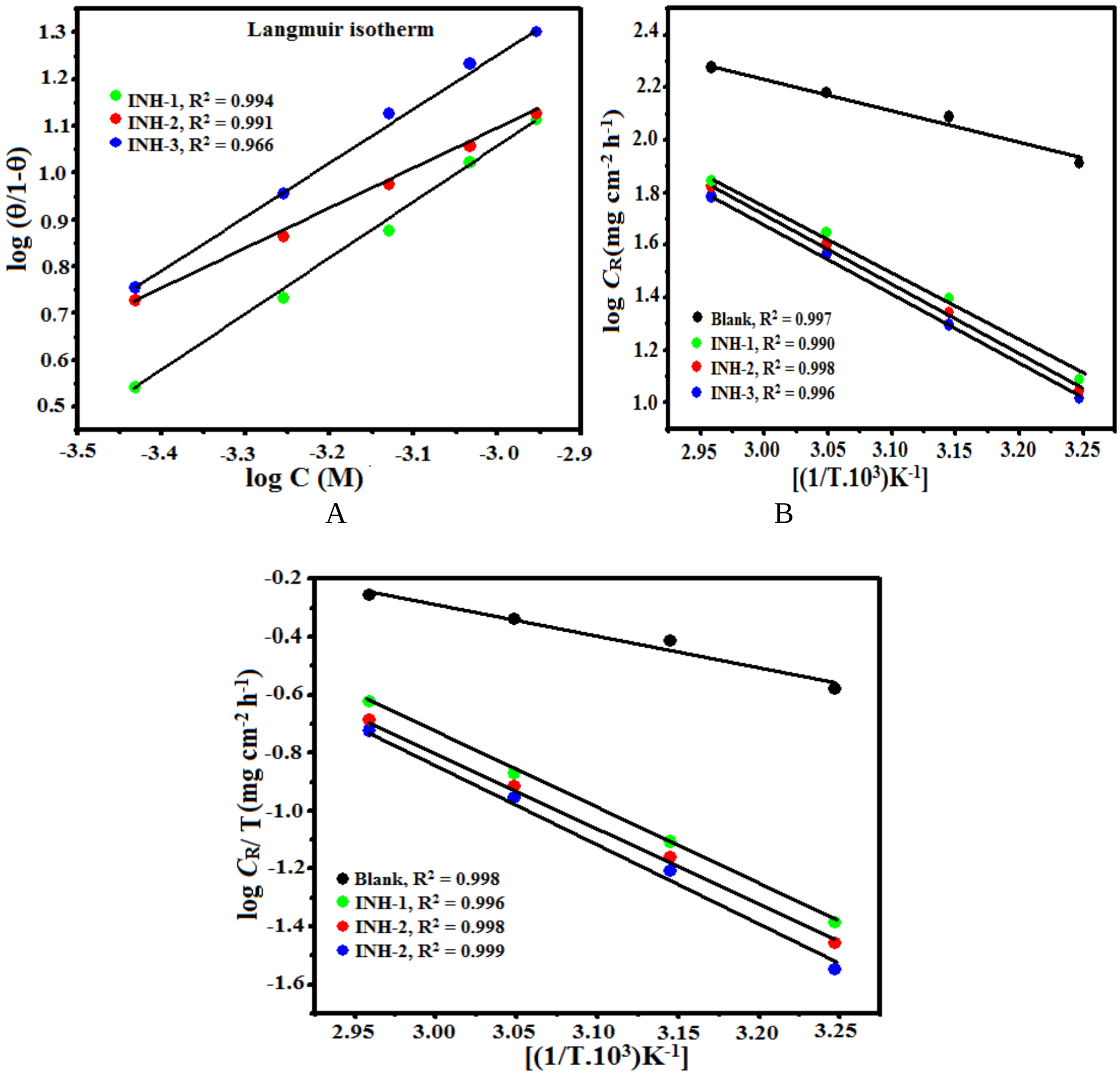

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Figure 2.(a-c) (a) Langmuir adsorption isotherm (b) Arrhenius plot of log C_R Vs 1/T (c) Arrhenius plot of log C_R/T Vs $1/T$

So the adsorption of organic inhibitors molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase [$Org_{(sol)}$] and water molecules at the electrode surface .[$H_2O_{(ads)}$] [27].

$$Org_{(sol)} + xH_2O_{(ads)} \longleftrightarrow Org_{(ads)} + xH_2O_{(sol)}$$

where x is the size ratio, that is, the number of water molecules replaced by one organic chalcones.

It has been reported by number of authors [28–30] that in acid solution, logarithm of the corrosion rate is a linear function with 1/T (Arrhenius equation):

$$\log(C_{\mathrm{R}}) = \frac{-E_{\mathrm{a}}}{2.303RT} + \log\lambda$$

where E_a is activation energy for the corrosion of Mild Steel in 1 M HCl, λ pre-exponential factor, R is the gas constant, A the Arrhenius pre-exponential factor and T is the absolute temperature. The Arrhenius plots for mild steel immersed in 1M HCl in chalcones-free and with chalcones solution is depicted in Figure 2 (b). The plots obtained were straight lines and apparent activation energies (E_a) at optimum concentration of chalcones were determined by linear regression between log C_R vs. 1/T and listed in Table 3. All the linear regression coefficients are close to unity. The data shows that thermodynamic activation functions (E_a) of the corrosion in mild steel in 1 M HCl solution in the presence of the chalcones is higher than those in free acid solution indicating that all the chalcones lowers the inhibition efficiency at higher temperature [31-33].The dependency of corrosion rate can also explain by transition stat equation [34].

$$C_{\mathrm{R}} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right)$$

where E_a apparent activation energy, k the pre-exponential factor, ΔH^* the apparent enthalpy of activation, ΔS^* the apparent entropy of activation, h is Planck's constant and N is the Avogadro number, respectively.

The relationship between $\log(C_R/T)$ and $1/T$ are shown in Figure2 (c). Straight lines are obtained with a slope $(-\Delta H^*/2.303R)$ and an intercept of $[\log(R/Nh)$ +, $(\Delta S^*/2{:}303R)$, from which the value of ΔH^* and ΔS^* were calculated and presented in Table 3.

Table 2. Thermodynamic parameters for mild steel in 1M HCl in absence and presence of optimum concentration of investigated chalcone.

Inhibitor	E_a (kJ mol^{-1})	ΔH^*(kJ mol^{-1})	ΔS^*(J K^{-1} mol^{-1})	ΔG^0(kJ mol^{-1})
Blank	28.48	26.04	-148.9	………
INH-1	49.40	50.36	-60.68	-32.85
INH-2	52.49	51.93	-59.56	-34.37
INH-3	57.48	54.38	-50.23	-34.92

Study of Table 2. reveals that the ΔH^* values for dissolution of mild steel in 1M HCl in presence of chalcones are higher (50.36–54.38 kJ mol^{-1}) than that in absence of inhibitors (26.04 kJ mol^{-1}).The positive sign of enthalpy reflect the endothermic nature of mild steel dissolution process meaning that dissolution of mild steel is difficult in presence of chalcones as compare in absence of chalcones [35]. On comparing the values of entropy of activation (ΔS*) listed in Table 2, it is clear that entropy of activation increased in presence of the studied chalcones compared to free acid solution. Such variation is associated with the phenomenon of ordering and disordering of inhibitors molecules on the mild steel surface. The increased entropy of activation in the presence of chalcones indicated that disorderness is increased on going from reactant to activated complex on metal/solution interface [36, 37].

The standard free energy of adsorption, (ΔG°_{ads}) at different temperatures were calculated using following formula and given in table 3.

$$\Delta G^{o}_{ads} = -RT\ln(55.5K_{ads})$$

The value 55.5 in this case is the concentration (M) of water in solution [38]. The negative values of ΔG^{o}_{ads} ensure the spontaneity of adsorption process and stability of the adsorbed layer on the mild steel surface. Generally, the values of around -20 kJ mol^{-1} or lower are consistent with physisorption, while those around-40 kJ mol^{-1} or higher involve chemisorption [39].

3.2 Electrochemical measurements

3.2.1. Potentiodynamic polarization measurements

Polarization measurements were carried out in order to gain knowledge concerning the kinetics of the cathodic and anodic reactions. Figure 3 represents the cathodic and anodic curves for three chalcones at optimum concentration in 1M HCl. It could be observed that both the cathodic and anodic reactions were suppressed with the addition of chalcones, which suggested that the chalcones reduced anodic dissolution and also retarded the hydrogen evolution reaction. The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (E_{corr}), corrosion currents densities (I_{corr}) and Tafel slopes (β_a, β_c) were calculated by extrapolating the Tafel slope and are listed in Table 4.The potentiodynamic study reveal that INH-3 maximum inhibition efficiency of 96.3% at 300 ppm concentration.

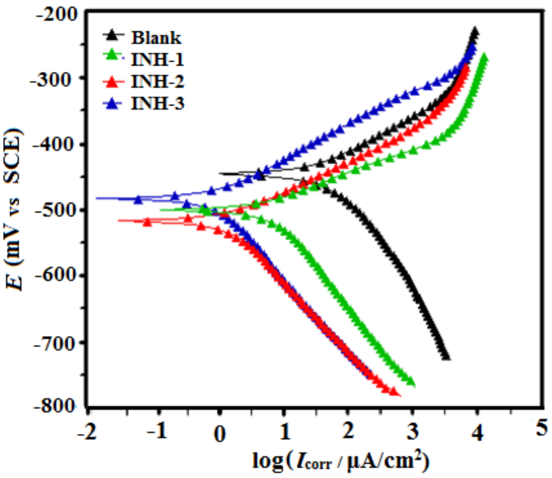

Figure 3. Tafel polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of optimum concentrations of chalcones

According to Ferreira and others [40-41], if the displacement in (E_{corr}) values:

(i) >85 mV in inhibited system with respect to uninhibited, the inhibitors could be recognized as cathodic or anodic type and

(ii) if displacement in Ecorr is <85 mV, it could be recognized as mixed-type.

For studied chalcones, the maximum displacement range was 14-21 mV towards cathodic region, which indicates that all studied chalcones are mixed-type inhibitors [42]. The values of corrosion current density (Icorr) decreased in presence of chalcones which suggests that the rate of electrochemical reaction was reduced due to the formation of a barrier layer over the mild steel surface by the chalcones molecule. From Table 3, it is also clear that the values of cathodic and anodic Tafel slope constant are changed in the presence of chalcones. This suggest that studied chalcones were first adsorbed onto the metal surface and impeded by merely blocking the reaction sites of the metal surface without affecting the anodic and cathodic reaction[43].

Table 3. The potentiodynamic polarization parameters and corresponding efficiencies of chalcones in 1 M HCl at optimum concentration

Tafel data							
Inhibitor	*Conc ppm*	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV/SCE)	β_a (mV/dec)	β_c (mV/dec)	θ	$\eta\%$
Blank	0.0	1150	-495	70.5	114.6	….	…..
INH-1	300	80.2	-502	45.9	132	0.9303	93.03
INH-2	300	65.4	-516	59.3	133.3.	0.9431	94.31
INH-3	300	35.4	-481	75.7	222.2	0.9692	96.92

3.2.2 Electrochemical Impedance Spectroscopy

Impedance spectroscopy provides information about the kinetics of the electrode processes and also about the surface properties of the investigated systems. The shape of impedance curves gives mechanistic information. Nyquist plots of mild steel in absence and presence of different concentrations of chalcones are shown in Figure 4. The inspection of the Figure 4, reveals that diameter of semi-circle loop i.e. impedance increases from INH-1 to INH-3 as a result increase in the inhibition efficiency [44]. The double layer capacitance (C_{dl}) in absence and presence of optimum concentration of chalcones was calculated by using following equation [45]:

$$C_{dl} = Y_0 (\omega_{max})^{n-1} \qquad (13)$$

where, Y_0 is CPE coefficient, n is CPE exponent (phase shift), ω is the angular frequency. The ω_{max} represents the frequency at which the imaginary component reaches a maximum.

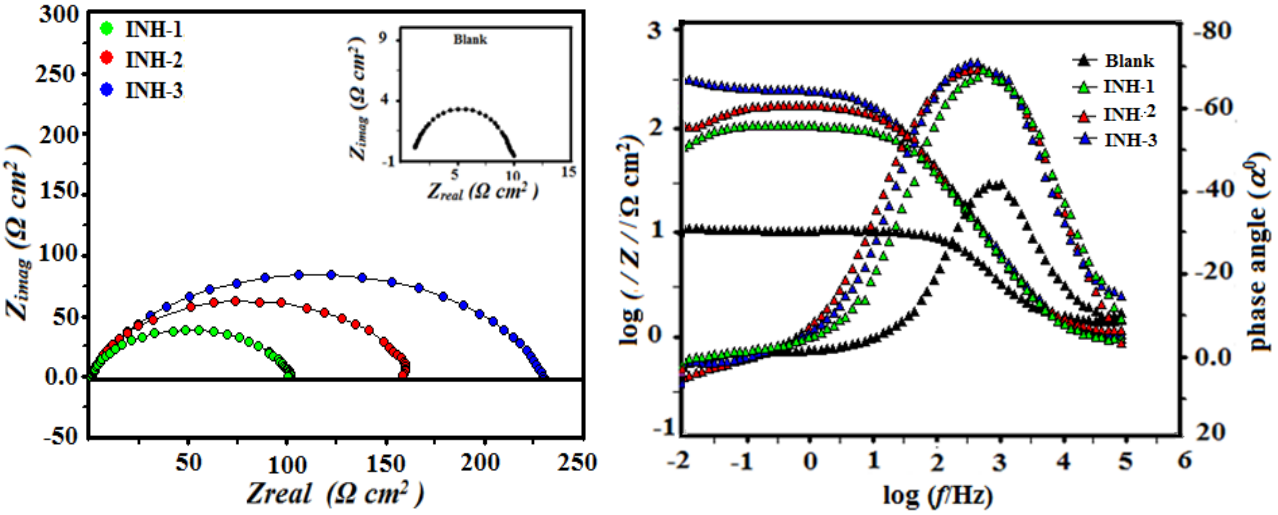

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Figure 4. (a) Nyquist plot in absence and presence of optimum concentrations of chalcones (b) Bode plot in absence and presence of optimum concentrations of chalcones

The EIS parameters such as R_s, Y_0, R_{ct} and C_{dl} were derived from the Nyquist plot are given in Table 4. It is clear from the result that the value of R_{ct} increases from 11.8 Ω cm^2 (Blank) to (98.93 – 258.13 µF cm^{-2}) in presence of optimum concentration of chalcones. It is also depicted that value of C_{dl} decreases from106.2 µF cm^{-2} (Blank) to 92.89-81.45 µF cm^{-2} in presence of 300 ppm concentration of chalcones. The decrease in capacitance (C_{dl}) on addition of inhibitor may be due to increase in local dielectric constant and/or may be due to increase in the thickness of the double layer, showing that chalcones inhibited mild steel corrosion by adsorbing at the metal/acid interface [46].

Table 4. The Electrochemical Impedance parameters and corresponding efficiencies of chalcones in 1 M HCl at optimum concentration.

Inhibitor	Conc	R_s (Ω)	R_{ct} (Ω cm^2)	n	Y_0 (µF cm^{-2})	C_{dl} (µFcm^{-2})	θ	η%
Blank	0.0	1.12	11.8	0.827	249.8	106.21	….	….
INH-1	300	0.86	98.93	0.860	135	92.89	0.9462	92.66
INH-2	300	0.95	157.05	0.864	100	79.37	0.9542	95.37
INH-3	300	0.87	258.13	0.836	92	81.45	0.9582	97.18

4. MECHANISM OF INHIBITION

Corrosion inhibition of mild steel in 1M HCl by chalcones can be explained on the basis of molecular adsorption of chalcones on to the mild steel surface. It is generally considered that the first step in the corrosion inhibition of a metal is the adsorption of the chalcones molecules at metal / solution interface [47].

Thus chalcones can adsorb on the mild steel surface by following ways:

(a) Electrostatic interaction between the charged molecules and charged metal;

(b) Interaction of π-electrons with the metal;

(c) Interaction of unshared pair of electrons in the molecule with the metal; and

(d) The combination of the all the effects [48-50].

Concerning inhibitors, the inhibition efficiency depends on several factors; such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface and the formation of metallic complexes. The order of inhibition efficiency of chalcones is as follows:

INH-3 > INH-2 > INH-1

The adsorption of organic inhibitor cannot be considers as purely physical or purely chemical phenomenon. The adsorption mechanism is influenced by nature and charge on metal surface and chemical structure of inhibitors. The charge on metal surface is due to electric field which emerges at the metal/electrolyte interface. It is well-known that mild steel specimens are positively charged with respect to the potential of zero charge (*PZC*) in acid solutions [51]. It is a well-known fact that the inhibitors not only offer electrons to metal atoms but also have unoccupied higher energy orbital to accept electrons from d-orbital of Fe atom for strengthening of bonding interaction [52,53]. A schematic illustration of different modes of adsorption of chalcones on metal/acid interface is shown in Figure 5.

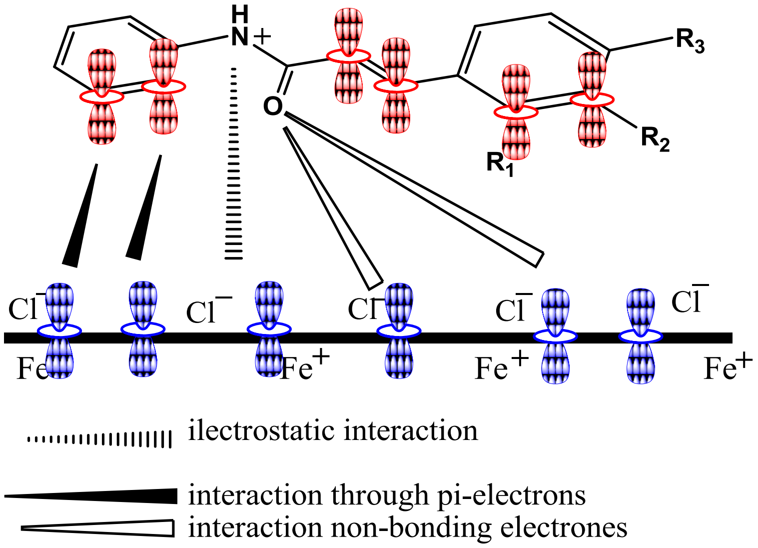

Figure 5. The schematic illustration of different modes of adsorption by chalcone on mild steel 1 M HCl interface

In aqueous solution of 1M HCl chalcones molecules may adsorb through protonated heteroatoms and already adsorbed Cl^- on mild steel surface. Initially, the protonated form of chalcone molecules in acid medium start competing with H^+ ions for electrons on mild steel surface. After release of H_2 gas, the cationic form of inhibitors returns to its neutral form and heteroatoms with free lone pair electrons promote chemical adsorption. Thus, there is a synergism between the adsorbed Cl^- ions and protonated chalcone. Hence, we can assume that the inhibition of mild steel corrosion in 1 M HCl is due to the adsorption of chalcones on the mild steel surface.

5. CONCLUSIONS

From above study it is concluded that:

1. Chalcones are good corrosion inhibitors for corrosion of mild steel in 1M HCl solution. The maximum efficiency was found to be 96.3% at 300 ppm concentration.
2. The adsorption of chalcones molecule on mild steel surface obeyed the Langmuir isotherm.
3. The Potentiodynamic studies reveal that chalcones are mixed type inhibitors i.e. it affected both cathodic and anodic reactions.
4. The negative values of ΔG shows that adsorption of inhibitors on mild steel is a spontaneous process.
5. The results obtained from weight loss and electrochemical methods are in good agreement.

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