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# Chitin as a Corrosion Inhibitor of Carbon Steel in HCl Solution

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**ABSTRACT**

*The inhibition ability of chitin (CH) for carbon steel corrosion in a 1.0 M HCl solution at 298K was studied by means of weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) technique. Polarization curves revealed that CH is a mixed-type inhibitor. EIS results show that the change in the impedance parameters ($R_t$ and $C_{dl}$) with concentration of CH is indicative of the adsorption of molecules leading to the formation of a protective layer on the surface of carbon steel. Results showed that CH is a good inhibitor for the corrosion of carbon steel in 1.0 M HCl solution and inhibition efficiency is higher than 96% at $1\times10^{-4}$ M of CH. Results indicate that the inhibition efficiencies increased with the concentration of CH. Adsorption of the inhibitor on the carbon steel surface followed Langmuir adsorption isotherm and the value of the free energy of adsorption, $\Delta G_{ads}$ indicated that the adsorption of CH molecule was a spontaneous process.*

**Keywords:** Corrosion inhibition, EIS, Steel, Polarization curves.

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## INTRODUCTION

Chitin is naturally produced polymers in many crustaceous; arthropods and cephalopods as well as in certain fungi forming the principal fibrillar polymer of their cell walls, thus coming after cellulose in its abundances [1]. It can be extracted from shrimp shells by chemical and biological methods with an advantages goes to biological ones [2-5]. In fact chitin has many pharmaceutical and biomedical applications, due its biodegradability [6-10].

Corrosion may be defined as a destructive phenomena, chemical or electrochemical, which can attack any metal or alloy through reaction by the surrounding environment and in extreme cases may cause structural failure. Corrosion can be also defined as the deterioration of material by reaction to its environment. The corrosion occurs because of the natural tendency for most metals to return to their natural state. The importance of corrosion studies is two folds. The first is economic; the second is conservation, applied primarily to metal resources. Corrosion control can be achieved by many methods, from which the use of corrosion inhibitors is one of the most effective alternatives [11]. An examination of the literature on corrosion inhibitors reveals that most organic inhibitors contain nitrogen, oxygen, sulfur and/or aromatic ring in their molecular structure [12-24]. The target of this work is to study the inhibition action of chitin (CH), on the corrosion of carbon steel in hydrochloric acid. Weight loss, electrochemical

impedance spectroscopy (EIS) and potentiodynamic polarization measurements, were used for the study. The molecular structure of chitin is shown in Fig. 1 below.

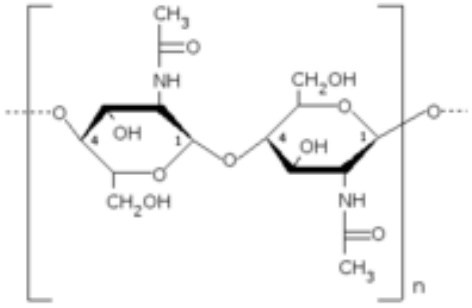


**Figure 1. Structure of Chitin (CH) molecule**

## MATERIALS AND METHODS

*2.1. Materials*

The steel used in this study is a carbon steel (CS) (Euronorm: C35E carbon steel and US specification: SAE 1035) with a chemical composition (in wt%) of 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu and the remainder iron (Fe).

*2.2. Solutions*

The aggressive solutions of 1.0 M HCl were prepared by dilution of analytical grade 37% HCl with distilled water. The inorganic compound tested is Chitin $(C_8H_{13}O_5N)_n$. The concentration range of this compound was $10^{-4}$ to $10^{-7}$ M.

*2.3. Weight loss measurements*

Coupons were cut into 2 × 2 × 0.08 $cm^3$ dimensions are used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 320, 800, 1200 grades of emery papers. The specimens were washed thoroughly with bi-distilled water, degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 80 mL. The immersion time for the weight loss is 6 h at 298 K.

*2.4. Polarization measurements*

*2.4.1. Electrochemical impedance spectroscopy*

The electrochemical measurements were carried out using Volta lab (Tacussel- Radiometer PGZ 100) potentiostate and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode of surface area of 0.094 $cm^2$. The working electrode was carbon steel. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solution for 30 minutes to a establish steady state open circuit potential (*E*ocp). After measuring the *E*ocp, the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The EIS experiments were conducted in the frequency range with high limit of 100 kHz and different low limit 0.1 Hz at open circuit potential, with 10 points per decade, at the rest potential, after 30 min of acid immersion, by applying 10 mV ac voltage peak-to-peak. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the *x*-axis.

The inhibition efficiency of the inhibitor was calculated from the charge transfer resistance values using the following equation [25]:

$$\eta_z\% = \frac{R_{p(inh)} - R_p}{R_{p(inh)}} \times 100 \quad (1)$$

where, $R_p$ and $R_{p\ (inh)}$ were the values of polarization resistance in the absence and presence of inhibitor, respectively.

*2.4.2. Potentiodynamic polarization*

The electrochemical behaviour of carbon steel sample in inhibited and uninhibited solution was studied by recording anodic and cathodic potentiodynamic polarization curves. Measurements were performed in the 1.0 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential automatically from -800 to -200 mV versus corrosion potential at a scan rate of 1 mV $s^{-1}$. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities ($I_{corr}$). From the polarization curves obtained, the corrosion current ($I_{corr}$) was calculated by curve fitting using the equation:

$$I = I_{corr}\left[exp\left(\frac{2.3\Delta E}{\beta_a}\right) - exp\left(\frac{2.3\Delta E}{\beta_c}\right)\right] \quad (2)$$

The inhibition efficiency was evaluated from the measured $I_{corr}$ values using the relationship:

$$\eta_{Tafel}\% = \frac{I^{\circ}_{corr} - I^{i}_{corr}}{I^{\circ}_{corr}} \times 100 \quad (3)$$

where, $I^{\circ}_{corr}$ and $I^{i}_{corr}$ are the corrosion current density in absence and presence of inhibitor, respectively.

## RESULTS AND DISCUSSION

*3.1. Electrochemical impedance spectroscopy measurements*

The impedance spectra for carbon steel in 1.0 M HCl solution without and with various concentrations of CH are presented as Nyquist plots in Fig 2. From these plots, the impedance response of mild steel has significantly changed on addition of the CH. For analysis of the impedance spectra containing a depressed capacitive semi circle [26].

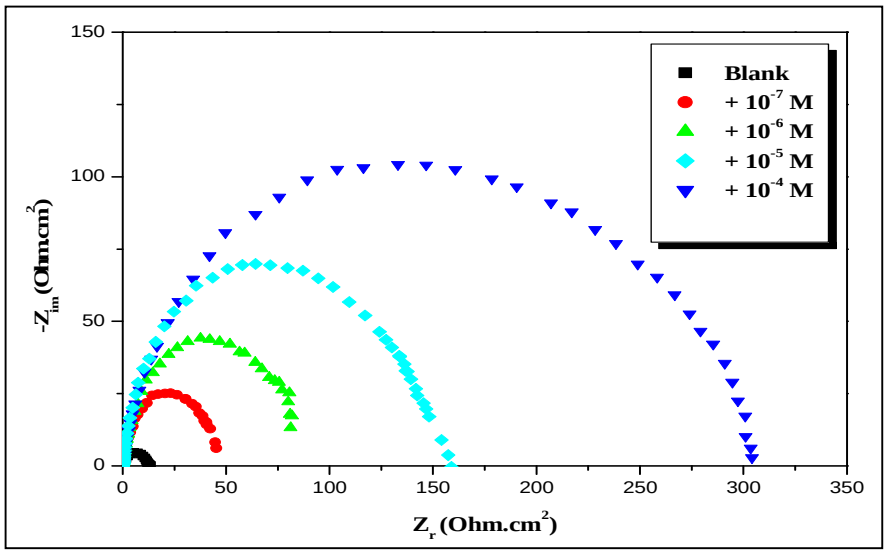


**Figure 2. Nyquist diagrams for C38 steel electrode with and without CH at $E_{corr}$ after 30 min of immersion**

The depression in Nyquist semicircles is a feature for solid electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogenities of the solid electrode [27,28]. Increasing the inhibitor concentration will increase the size of the curves, indicating the time constant of the charge transfer and double-layer capacitance [29]. This behaviour shows the adsorption of CH on carbon steel surface. It is also found that from the Nyquist plots, even with the addition or absence of inhibitor does not alter the style of impedance curves, thus

proposing a similar mechanism of inhibition is involved. The impedance parameters derived from these plots are given in Table 1. As noted from Table 1, the polarization resistances values containing inhibitor substantially increased along the concentration compared to that without inhibitor. It is also clear that the value of $C_{dl}$ decreases on the addition of inhibitor, indicating a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting the inhibitor molecules function by the formation of the protective layer at the metal surface.

**Table 1. Electrochemical Impedance parameters for corrosion of steel in acid medium at various contents of CH**

| Inhibitor | **Con. (M)** | $R_t$ ($\Omega.cm^2$) | $C_{dl}$ ($\mu F/cm^2$) | $\eta_z$ (%) |
|---|---|---|---|---|
| **Blank** | 0.00 | 12 | 88.46 | - |
| **CH** | $10^{-4}$ | 310 | 7.02 | 96.12 |
| | $10^{-5}$ | 150 | 10.90 | 92.10 |
| | $10^{-6}$ | 78 | 25.51 | 84.61 |
| | $10^{-7}$ | 49 | 38.23 | 75.51 |

*3.2. Polarization curves*

Fig.3 shows the potentiodynamic polarization curves after the addition of corrosion inhibitor CH. In every curve, it is observed that the current densities of the anodic and cathodic branch are displaced towards lower values. This displacement is more evident with the increase in concentration of the corrosion inhibitor when compared to the blank material.

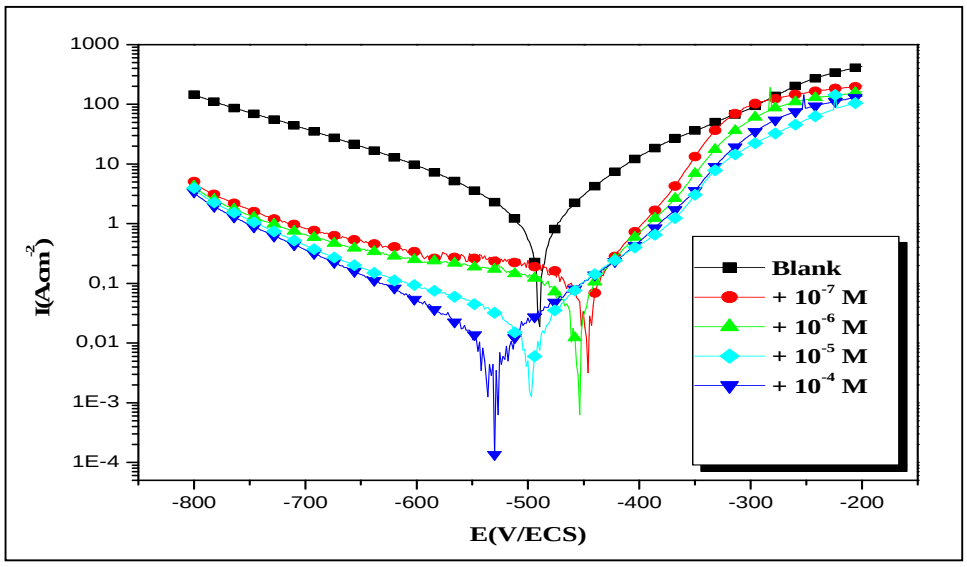


**Figure 3. Potentiodynamic polarization curves of C38 steel in 1M HCl in the presence of different concentrations of CH**

The corrosion parameters extracted from polarization curves containing corrosion current density ($I_{corr}$), corrosion potential ($E_{corr}$), the cathodic Tafel slopes ($bc$), inhibition efficiency ($\eta_{Tafel}$ %) have been calculated as a function of CH concentration according to equation (3) [30, 31] and have been presented in Table 2. From table 2, the corrosion current density decreased with the increase of the inhibitor concentration and E % showed the opposite trend which indicated that the inhibitor suppressed the carbon steel corrosion in 1.0 M HCl solution. The presence of CH resulted in no definite trend in the shift of $E_{corr}$ compared to that in the absence of CH, however, the displacement in $E_{corr}$ is < 85 mV. These results indicated that the presence of CH inhibited both iron oxidation and hydrogen evolution, consequently CH can be classified as mixed corrosion inhibitor [32-34] with the inhibitory action caused by a geometric blocking effect [35]. In addition, the inhibitory action was due to a reduction of the reaction area on the surface of the corroding metal [36].

**Table 2. Electrochemical parameters of C38 steel at various concentrations of CH in 1M and corresponding inhibition efficiency.**

| Inhibitor | Conc. (M) | -$E_{corr}$ (mV/SCE) | $I_{corr}$ (μA/cm$^2$) | -$b_c$ (mV/dec) | $\eta_{Tafel}$ (%) |
|---|---|---|---|---|---|
| Blank | 0.00 | 492 | 226 | 158 | - |
| CH | $10^{-4}$ | 530 | 12 | 118 | 94.69 |
| | $10^{-5}$ | 497 | 20 | 140 | 91.15 |
| | $10^{-6}$ | 454 | 45 | 182 | 80.08 |
| | $10^{-7}$ | 442 | 64 | 183 | 71.68 |

*3.3. Weight loss measurements*

*3.3.1. Effect of concentration*

Weight loss experiments were done according to the method described previously [37]. Weight loss measurements were performed at 298 K for 6 h by immersing the carbon steel coupons into acid solution (80 mL) without and with various amounts of inhibitor. After the elapsed time, the specimen were taken out, washed, dried and weighed accurately.

The inhibition efficiency ($\mu_{WL}$%) and surface coverage (θ) was determined by using following equations:

$$\mu_{WL}\% = \frac{w_0 - w_i}{w_0} \times 100 \quad (4)$$

$$\theta = \frac{w_0 - w_i}{w_0} \quad (5)$$

where, $w_0$ and $w_i$ are the weight loss value in the absence and presence of inhibitor.

Initially carbon steel corroded at higher rate in acid but presence of inhibitor retarded the corrosion rate and remarkable improvement in inhibition efficiency was achieved (Figure 4). It was observed from Figure 4 that corrosion rate was decreasing with increasing inhibitor concentration whereas inhibition efficiency was increased with increasing amount of inhibitor. From data listed in Table 3 decreased value of weight loss was noticed with increasing concentration of inhibitor due to increased surface coverage which can be accounted for inhibitive action of inhibitor.

**Table 3: Effect of CH concentration on corrosion data of carbon steel in 1.0 M HCl**

| Inhibitor | Conc (M) | $C_R$ (mg cm$^{-2}$ h$^{-1}$) | $\mu_{WL}$(%) | θ |
|---|---|---|---|---|
| Blank | 1.0 | 1.0023 | - | - |
| CH | $10^{-4}$ | 0,02796 | 97.21 | 0,9721 |
| | $10^{-5}$ | 0,09161 | 90.86 | 0,9086 |
| | $10^{-6}$ | 0,17399 | 82.64 | 0,8264 |
| | $10^{-7}$ | 0,26540 | 73.52 | 0,7352 |

*3.4. Adsorption isotherm and thermodynamic*

The action of an inhibitor in aggressive acid media is assumed to be due to its adsorption at the metal/solution interface. The adsorption process depends on the electronic characteristics of the inhibitor, the nature of metal surface, temperature, steric effects and the varying degrees of surface-site activity [38,39]. In fact, the solvent $H_2O$ molecules could also be adsorbed at the metal/solution interface. Therefore, the adsorption of organic inhibitor molecules from the aqueous solution can be considered as a quasi substitution process between the organic compounds in the aqueous phase $Org_{(sol)}$ and water molecules at the electrode surface $H_2O_{(ads)}$ [40]:

$$Org_{(sol)} + xH_2O_{(ads)} \leftrightarrow xH_2O_{(sol)} + Org_{(ads)} \quad (6)$$

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

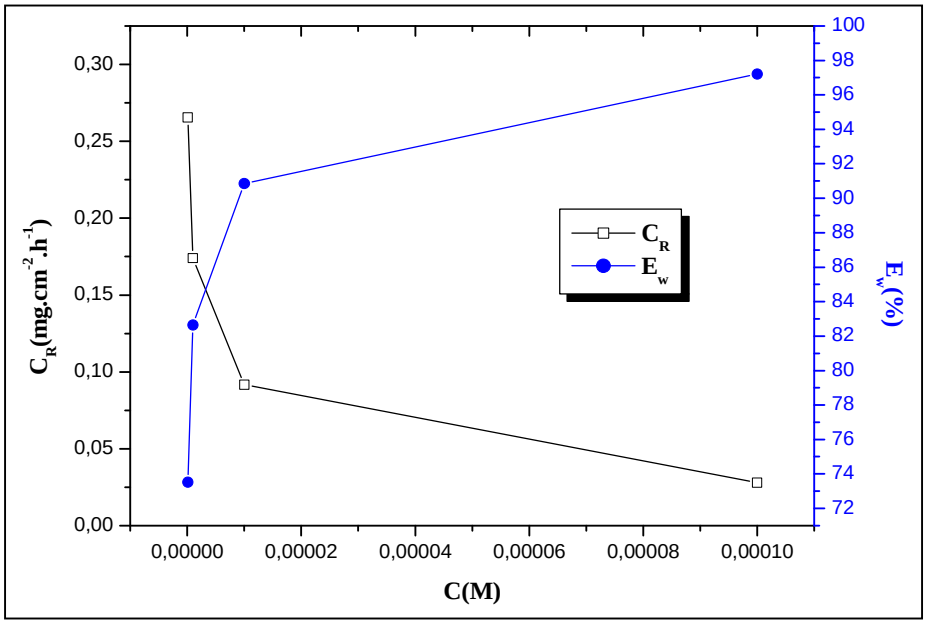


**Figure 4. Variation of inhibition efficiency and corrosion rate in 1M HCl on C38 steel surface without and with different concentrations of CH**

The type of the adsorption isotherm can provide additional information about the properties of the tested compounds. In order to obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitor must be calculated. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media have been evaluated from the weight loss measurements and listed in Table 4. Attempts were made to fit the θ values to various isotherms, including Langmuir, Temkin, Frumkin and Flory-Huggins. By far, the best fit is obtained with the Langmuir isotherm. Langmuir adsorption isotherm is described by the following equations:

$$\frac{\theta}{1-\theta} = K_{ads} C_{inh} \tag{7}$$

By rearranging this equation:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \tag{8}$$

where, $C_{inh}$ is the inhibitor concentration, $K_{ads}$ is the adsorption equilibrium constant and θ is the surface coverage. Fig.5 shows the plots of Cinh/θ versus $C_{inh}$ and the expected linear relationship is obtained for CH. The strong correlations ($R^2$ = 0.9995) confirm the validity of this approach. The slope of the straight line ($K_{ads}$) has been found to be 4.85 x$10^6$ $M^{-1}$ (Table 4) suggesting that the adsorbed inhibitor molecules form monolayer on the carbon steel surface and there is no interaction among the adsorbed inhibitor molecules [41]. On the other hand, the relatively high value of adsorption equilibrium constant reflects the high adsorption ability of CH on carbon steel surface [42,43]. The standard free energy of adsorption ($\Delta G^{\circ}_{ads}$) can be given as the following equation:

$$\Delta G^{\circ}_{ads} = -RTLn(55.5K_{ads}) \tag{9}$$

where, R is the gas constant (8.314 J $K^{-1}$ $mol^{-1}$), T is the absolute temperature (K), the value 55.5 is the concentration of water in solution expressed in 1 M [44].

**Table 4. Thermodynamic parameters for the adsorption of CH in 1.0 M HCl on the carbon steel at 298K**

| Inhibitor | Slope | $K_{ads}$ ($M^{-1}$) | $R^2$ | $\Delta G^{\circ}_{ads}$ (kJ/mol) |
|---|---|---|---|---|
| CH | 2.06075 x$10^{-7}$ | 4.85 x$10^{6}$ | 0.99 | -48.068 |

The $\Delta G^{\circ}_{ads}$ value is calculated as -48.068 kJ $mol^{-1}$. Generally, the values of $\Delta G^{\circ}_{ads}$ up to -20 kJ $mol^{-1}$ are consistent with the electrostatic interaction between the charged molecules and the charged metal (physical adsorption) while those more negative than 40 kJ $mol^{-1}$ involve sharing or transfer of electrons from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (chemisorption) [45,46]. In this study, the value of $\Delta G^{\circ}_{ads}$ is slightly negative than -20 kJ $mol^{-1}$; which suggests that the adsorption mechanism of the CH on steel in 1.0 M HCl solution is mainly the physical adsorption [47-49]. However, adsorption of inhibitor molecules is not merely physisorption or chemisorption, and it includes a comprehensive adsorption (physical and chemical adsorption) for the same values [50].

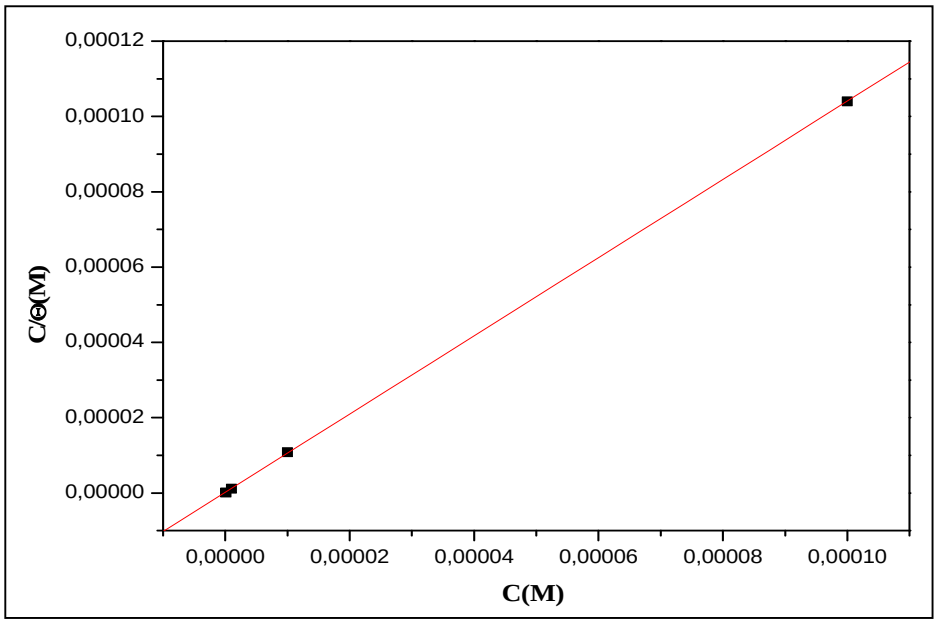


**Figure 5. Langmuir adsorption of CH on the carbon steel surface in 1.0 HCl solution**

## CONCLUSION

We have studied the inhibiting effect of chitin in 1M HCl on the carbon steel by using various methods. The results obtained are in good agreement and are given as follows. The presence of chitin reduces the corrosion rate of carbon steel in HCl medium, its inhibition efficiency increases with its concentration. Chitin acts as cathodic and anodic inhibitor and adsorbed on the carbon steel surface according to Lamgmuir isotherm model. The inhibition efficiency of chitin increased with the concentration and reached a maximum at $10^{-4}$ M.

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