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Influence of furfuraldehyde derivatives as corrosion inhibition of mild steel in hydrochloric acid solution

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Abstract

Furfuraldehyde derivatives have been prepared by the condensation reaction between furfuraldehyde with urea (*CFU*) & furfuraldehyde with thiourea (*CFTU*). The products were subjected to corrosion inhibition studies on mild steel in hydrochloric acid solution using chemical and electrochemical methods. The maximum inhibition efficiency of 88.09 in case of *CFU* and 90.47 in case of (*CFTU*) were observed in optimum 5 X 10^{-3} M/L concentration inhibitor. Results also showed that the prepared compounds control the corrosion of mild steel in hydrochloric acid solution. The *CFTU* showed better corrosion inhibition than *CFU*. Nevertheless, both these compounds possessed good interaction with the metal surface and formed a barrier between metal and solution interface. Various parameters such as, activation energy, enthalpy of activation, free energy of activation and entropy of activation were calculated and interpreted. The negative values of ΔG_{ads} showed the spontaneous adsorption of the inhibitor on the metal surface. The products control both anodic and catholic reactions and acts as mixed type of inhibitors. The calculated percentage inhibition efficiency obtained from both the methods nearly same. The mode of corrosion inhibition was explained on the basis of adsorption of the inhibitor on metal surface. Interaction of the inhibitors with the metal surface was assessed by FTIR technique and change of surface morphology was characterized by SEM technique.

1. Introduction

Mild steel is one of the most promising materials for the fabrication of various industrial equipment's. But it undergoes corrosion when exposed to corrosive environment and is the major drawback to use for a long period of time. However, when the material is in contact with the chloride ions in the corrosive medium, these ions induced the metals and alloys to undergo different forms of corrosion. Hydrochloric acid is the most commonly preferred acid for descaling, acid pickling and other industrial cleaning purpose [1-3]. Extreme care is taken to handle such an acid even at dilute concentration is also high corrosive towards many metals and alloys.

Many protective measures have been developed to minimize the corrosion of metals and alloys in acid medium such as Apricot juice as green corrosion inhibitor of mild steel in phosphoric acid [4], Peach juice as an anti-corrosion inhibitor of mild steel [5], and experimental modeling of inhibition's mechanism of Cupronickel Alloy by DETA and EDA into acid corrosive media were also developed recently [6]. Furthermore, the use of organic inhibitor is one of the significant methods of corrosion protection. Several synthetic organic compounds containing O, N & S in their functional groups were proven to effectively interact on the metal surface and control the corrosion of metals in acid solutions [7-9]. In addition to such organic compounds some heterocyclic compounds were also found to be very good corrosion inhibitors for mild steel in acid media which reported recently. The protection ability of the inhibitors related to molecular structure and number of adsorption centers available in the molecule, molecular size and availability of charge density, nature of the corrosive medium, nature of the metal surface, complex formation, nature of adsorption and metal surface area covered by the inhibitor [10, 11].

Many authors developed large number of Schiff base compounds these are more affinity to adsorbed on the metal surface due to the presence of rich electron densities on imine center (–C=N-) of the molecule and effectively control the corrosion of metals and alloys. The benefit of use of Schiff base as corrosion inhibitor is that they can be synthesized conventionally and easily using relatively cheap materials [12-19]. Hydrazones, anionic surfactants and amino acids have been developed as corrosion inhibitors for steel in acid medium. Imidazolium compounds were developed as corrosion inhibitors for copper, aluminum and to mild steel [20]. The roles of adsorptive inhibitors are to control the localized corrosion by opposing the adsorption of anions of the corrosive medium or by the formation of the thin oxide layer on the metal surface. The presence of both nitrogen and sulphur in the inhibitor showed enhanced adsorption process comparison with the molecule contained either nitrogen or Sulphur [21].

In the present study, condensation of furfuraldehyde with urea (*CFU*) and furfuraldehyde with thiourea (*CFTU*) were prepared and developed as corrosion inhibitors for mild steel in hydrochloric acidic medium. Emphases have given to variation of acid concentration, inhibitor concentration and temperature of the test solution on corrosion and corrosion inhibition processes. In views of this, serious attempts have made to synthesize such compounds which possess bis imine group which might show better inhibition efficiency which is described well in the present manuscript.

2.Expeerimental details

2.1. Samples preparation

Mild steel

Commercial grade mild steel (AISI 1079) composition (C= 0.5%, Mn = 0.5 %, S = 0.05 % and Fe = 98.95%) sheets of 0.2 cm thickness was selected for corrosion studies. For weight loss measurements, rectangular plates of exposed area 5 x 1 x 0.2 cm size were used and for electrochemical measurements, mild steel used as a working electrode of surface area 1 cm^2 was exposed and the remaining portion was covered with chemical resistant epoxy resin. The virgin article may be covered with scale or oxide film, heat scale, workshop soils, and oils, grease, dirt, rust on its surface. The metal surface free from all these impurities exhibits effective interaction with the inhibitor. Prior to use, the specimens were subjected for pretreatment process. Removal of extraneous materials is achieved in practice in three stages followed removal of heavy grease and oil, descaling and washing.

The articles were treated with trichloroethylene vapours in a closed vessel. This treatment removes heavy grease and oil present on the surface of the articles. Preliminary descaling was done by mechanical polishing and was followed by acid pickling in 5% sulphuric acid for 10 minutes at 323 K. The mild steel plates were given bright dip in a bath containing oxalic acid 25 gL^{-1}, sulphuric acid 0.1 mL L^{-1}, hydrogen peroxide (30%) 13 mL^{-1} and temperature 298 K. The treated samples were polished with a polishing machine and also using different grades of emery papers (320-2000), starting with the coarsest to the finest grade, until a mirror finish was obtained. The polished samples were washed with double distilled water and once again degreased in trichloroethylene and again washed with distilled water. Finally rinsed with acetone dried and immediately stored in desiccator.

Test solutions

Corrosive medium

Hydrochloric acid solution of 2 M was prepared and used as corrosive medium for mild steel.

Preparation of Inhibitors

The *urea bis furfural* (*CFU*) and *thiourea bis furfural* (*CFTU*) were synthesized and used as corrosion inhibitors. The condensation reactions between furfuraldehyde with urea (*CFU*) & furfuraldehyde with thiourea (*CFTU*) were carried out in a flask with stopcock. For the preparation of*CFU*, urea was dissolved in water and furfuraldehyde was added slowly with stirring, when furfuraldehyde was completely dissolved, HCl was incorporated into the solution. A brown solid began to precipitate after 30 min, depending on acid-concentration. The product was washed several times with water, until residues of the reactants were eliminated and dried. The purity of the compound was monitored by TLC. Similarly *CFTU* was also prepared and both the compounds were characterization by ^{1}HNMR.

^{1}H NMR (∂ ppm): 6.3-6.5 (m, 4H, Ar-H), 7.4 (m 2H – aldimineH), and 7.5-7.6 (s, 2H) spectral data of both the compounds. The formation of imine was confirmed by FTIR spectra. The characteristic stretching bands appeared at 1613.13 cm^{-1} in *CFU* and 1652.60 cm^{-1} in *CFTU* indicated the formation of imine (C=N) groups.

The structures of condensation products have shown in Figure 1. Using of it, different concentrations of inhibitor solutions were prepared in 2M HCl solution. All the test solutions were prepared using doubled distilled water with analytical grade chemicals supplied by Sisco Chem pvt ltd Mumbai, India.

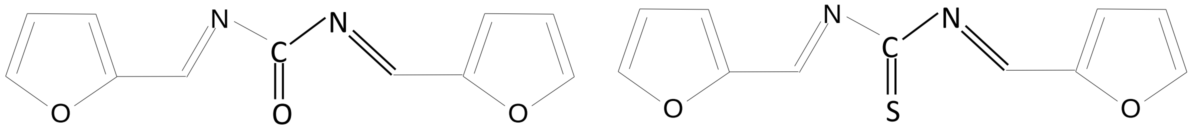


Figure 1: *urea bis furfural(CFU)* *thiourea bis furfural* (*CFTU*)

2.2. Weight loss measurements

Weight loss experiment was performed for the determination of corrosion rate and corrosion inhibition of mild steel in hydrochloric acid medium. The cleaned & dried specimens were weighed using electronic digital balance (Scale Tech) and suspended in a 100 mL beaker containing acid or acid solution with different concentration of inhibitor and kept in a thermostat. After the specified time of immersion, the specimen was removed, washed in running water, dried, placed in a desiccator to attain room temperature and weighed. All the experiments were carried out in duplicate and average weight loss were recorded. Corrosion rate (W_{corr}) of mild steel and percentage inhibition efficiency (% IE) were calculated using the following relations [22].

$$W_{corr} = \frac{\Delta m}{St} \qquad (1)$$

where Δm is the weight loss in mg, S is the surface area in cm^2 and‘t’ is the immersion period in hour.

$$\%IE = 1 - \frac{W^1_{corr}}{W_{corr}} \text{ x } 100 \qquad (2)$$

where, W_{corr} and W^1_{corr} are the rates of corrosion of mild steel in absence and presence of the inhibitor respectively.

2.3. Electrochemical measurements

Electrochemical measurements were performed at the CHI 608D electrochemical workstation at room temperature (301 ± 1K). For polarisation measurements, three electrode cell consists of mild steel used as a working electrode. Silver-silver chloride electrode and platinum were used as reference and counter electrodes respectively. Prior to each electrochemical measurement, steady-state open-circuit (OCP) potential of the working electrode was determined by immersed 30 minutes in a test solution. Current-potential curves measured with a 0.01 V s^{-1} scan rate in the potential range obtained by applying - 0.2 and + 0.2 V to the OCP value. Various parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic (β_c) and anodic (β_a) Tafel slopes were calculated. Using the corrosion current density, the *%IE* was calculated using the following relation [23].

$$\%\mathrm{IE} = 1 - \frac{I^1_{corr}}{I_{corr}} \text{x } 100 \qquad (3)$$

where, I_{corr} and I^1_{corr} are the corrosion current densities of mild steel without addition and with addition of inhibitor in hydrochloric acid medium respectively.

2.4. Adsorption isotherm & thermodynamic parameters

The nature of the corrosion inhibition was explained on the basis of adsorption of the inhibitors on mild steel surface and obeyed Langmuir adsorption isotherms. Various parameters like activation energy, heat of adsorption, free energy of adsorption and entropy of adsorption were calculated using the following relations [24].

Langmuir adsorption isotherm

$$\log \frac{\theta}{1-\theta} = \log K + \log C \qquad (4)$$

where θ = surface coverage, K = adsorption coefficient and C= concentration. The surface coverage was calculated using the relation [25].

$$\theta = \frac{W - W_0}{W} \qquad (5)$$

where, W and W_0 are the mass losses in the absence and presence of the inhibitors respectively.

Thermodynamic Parameters

In order to calculate activation thermodynamic parameters of the corrosion reaction such as activation energy (E_a^*), activated entropy (ΔS^*_a) and enthalpy (ΔH^*_a), the Arrhenius equation and its alternative formulation called transition state equation were employed.

$$W_{corr} = k \exp(-E_a^* / RT) \qquad (6)$$

$$W_{corr} = \frac{RT}{Nh} \exp\left[\frac{\Delta S^*_a}{R}\right] \exp\left[\frac{-\Delta H^*_a}{RT}\right] \qquad (7)$$

where W_{corr} is the corrosion rate, k is a constant depends on a metal type and electrolyte, E_a^* is the apparent activation energy, h is the Planck's constant (6.626176 x 10^{-34} J s), N is the Avogadro's number (6.02252 x10^{23} mol^{-1}), R is the universal gas constant and T is the absolute temperature, ΔH^*_a is the enthalpy of activation, and ΔS_a^* is entropy of activation. The free energy of adsorption (ΔG^0_{ads}) was calculated using the following relation [26, 27].

$$\Delta G_{ads} = -2.303\ RT \log (55.5K_{ads}) \quad (8)$$

$$K_{ads} = \frac{1}{C} \times \frac{\theta}{1-\theta} \quad (9)$$

where ‘θ’ be the surface coverage, ‘K_{ads}’ is adsorption constant, and ‘C’ is the inhibitor concentration.

2.5. Characterization

FTIR and SEM techniques

The corrosion control in presence of inhibitors was explained through adsorption process. The interaction & adsorption of these inhibitors on mild steel surface was confirmed by FT-IR spectra. The change in surface morphology of mild steel during corrosion and corrosion inhibition process was assessed by SEM technique.

3. Results and Discussion

3.1. Weight loss determination

The corrosion rate of mild steel in presence of different concentration of *CFU&CFTU* in 2M HCl at 301 ± 1 K are presented in Table 1. The corrosion rate in absence of the inhibitors is more due to the presence of large number of H^+ ions in acid solution, which enhances the rate of reduction reaction.

Table 1: W_{corr} and %IE in absence (blank) and presence of *CFU* and *CFTU* for mild steel in 2M HCl with 2 hours immersion period at 301 ± 1 K.

Conc. of inhibitors (M)	**W_{corr} (g cm^{2}h^{-1})**	**%IE**
Blank	0.021	----
	CFU	
0.001	0.013	38.09
0.002	0.009	57.14
0.003	0.005	76.19
0.004	0.003	85.71
0.005	0.0025	88.09
	CFTU	
0.001	0.011	47.61
0.002	0.007	65.71
0.003	0.004	80.95
0.004	0.0026	87.61
0.005	0.002	90.47

In addition of *CFU&CFTU* to the acid solution, the rate of corrosion of mild steel is decreased and the percentage inhibition efficiency (%IE) was increased with increasing inhibitors concentration. However maximum %IE was found to 88.09 and 90.47 in addition of 0.005M *CFU* & *CFTU* respectively. Further increased inhibitors concentration less improvement was noticed in %IE and 0.005 M is treated as the optimum concentration of the inhibitors [25]. In acid solution, the *CFU&CFTU* molecules are got protonated, these protonated molecules are influenced to decrease the rate of reduction reaction. Further the added inhibitor molecules are adsorbed on mild steel surface and form a thin layer which isolates the metal surface from the corrosive medium and control the corrosion of the mild steel [25].

3.2. Effect of immersion time

W_{corr} and %IE of inhibitors for mild steel in 2M HCl at different time intervals in optimum concentration of the inhibitors are presented in Table 2. The results showed that, in the presence of the inhibitors, the corrosion rate of mild steel was decreased and %IE was increased as the immersion period increased up to 4 hours. In presence of the inhibitors, as the immersion period increased a greater number of inhibitor molecules adsorbed and covered larger surface area and decrease the dissolution rate of the mild steel. The maximum %IE was attained to 94.21for *CFU* and 95.31 for *CFTU*. Further increase in the immersion time, no improvement in %IE was noticed [28].

Table 2: W_{corr} & %IE of *CFU* and *CFTU* for mild steel in 2 M HCl at 301 ± 1 K.

Time(h)	**W_{corr} (g cm^{2}h^{-1})**			**W_{corr} (g cm^{2}h^{-1})**	
	Blank	*CFU*	% IE	*CFTU*	% IE
01	0.016	0.0042	73.75	0.0040	75.00
02	0.021	0.0025	88.09	0.002	90.47
03	0.028	0.0024	91.42	0.0017	93.92
04	0.038	0.0022	94.21	0.0015	95.31

3.3. Effect of temperature

W_{corr} and % IE of *CFU* and *CFTU* for mild steel immersion period of 2 h in 2M HCl at different temperatures were investigated using weight loss method. The results showed that W_{corr} of mild steel increased as the temperature increased from 301 ± 1 K to 321 ± 1K. It is inferred that as the temperature increased, the migration of H^+ ions towards the mild steel surface was enhanced and induced to increase the rate of reduction reaction [29]. The %IE was decreased at higher temperature due to increase in desorption of the adsorbed molecule on the mild steel surface [30]. W_{corr} and % IE of mild steel at different temperatures were presented in Table 3.

Table 3: W_{corr} and % IE of *CFU* and *CFTU* for mild steel in 2M HCl immersion period 2 h at different temperatures.

Temperature (K)	**W_{corr}(g cm^{-2} h^{-1})**			**% IE**	
	Blank	*CFU*	*CFTU*	*CFU*	*CFTU*
301	0.021	0.003	0.0024	85.71	88.57
311	0.032	0.008	0.0068	75.00	78.75
321	0.053	0.016	0.015	69.81	71.68

Activation parameters of corrosion process

The corrosion rates evaluated at different temperatures in the absence and presence of inhibitors were used to calculate the activation energy of the metal dissolution. Arrhenius equation was used to calculate the apparent activation energy of corrosion process. Figure 2 shows the Arrhenius plots, using Arrhenius plots activation energy (E_a^*) for corrosion and corrosion inhibition processes for mild steel were calculated. Figure 3 shows the transition plots for mild steel corrosion in 2M HCl in absence and in presence of *CFU* & *CFTU*. The values of activation energy (E_a^*), enthalpy of activation (ΔH_o^*) and entropy of activation (ΔS_o^*) were calculated and presented in the Table 4. The data showed that the activation energy for the corrosion of mild steel in 2M HCl in the presence of inhibitor is higher than that of free acid. This indicated that the used inhibitors considerably increase the activation energy of the corrosion process due to their adsorption onto the metal surface. The higher activation energy value is associated with its physical adsorption. The increased activation energy in the presence of the inhibitor suggests that adsorbed inhibitors create a physical barrier to charge and mass transfer, leading to reduction in corrosion rate.

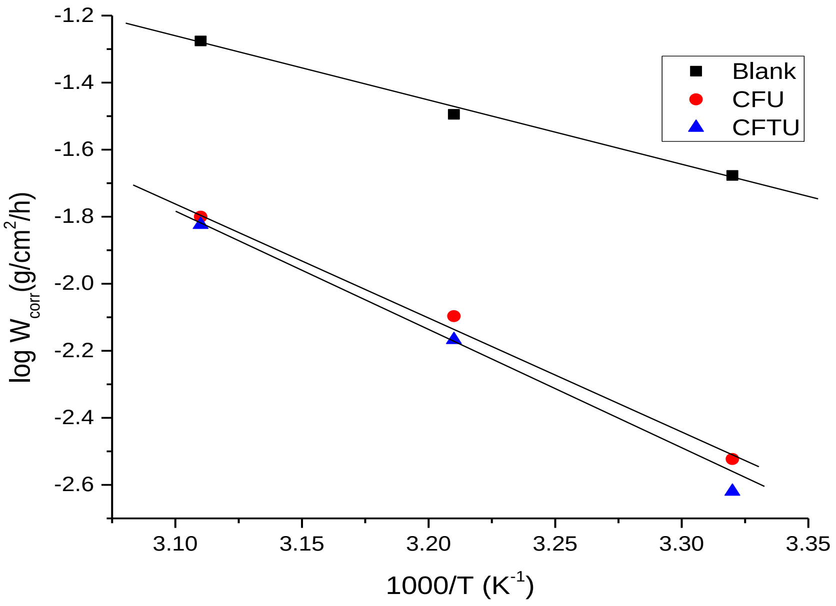


Figure 2: Arrhenius plots for mild steel in 2M HCl in absence and presence of inhibitors.

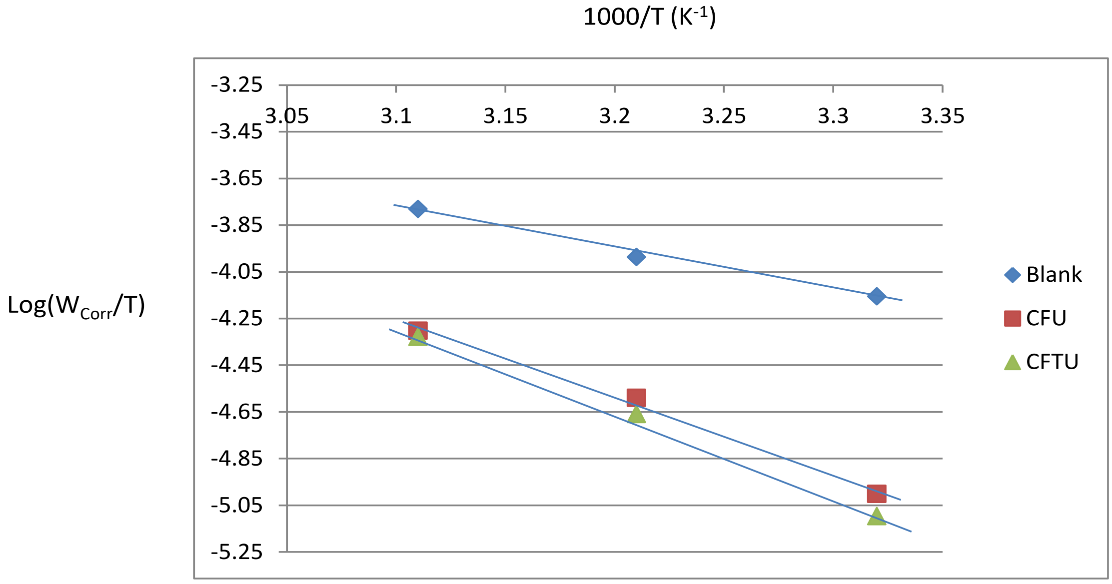


Figure 3: Transition plots for mild steel corrosion in 2M HCl in absence and of CFU & CFTU.

Table 4: Activation parameters of mild steel corrosion in the presence of *CFU* & *CFTU* in 2M HCl

Inhibitors	**E_a^* (kJ mol^{-1})**	**ΔH_0^* (kJ mol^{-1})**	**ΔS_0^* (kJ mol^{-1})**
Blank	36.03	33.94	-178.42
FUC	66.40	63.87	-81.001
FTUC	72.66	70.09	-62.28

The positive values of ΔH_o^* in the absence and presence of inhibitor reflect the endothermic nature of metal dissolution process, which suggested the slow dissolution of mild steel. It is evident from the table that the value of ΔH_o^* increased in the presence of inhibitors than the uninhibited solution indicating higher protection efficiency. The values of ΔS_o^* showed that the entropy of activation decreased in the presence of inhibitor than that of the free acid. It indicated that low value of ΔS_o^* supports the slower metal dissolution in the presence of *CFU* & *CFTU*.

3.4. Electrochemical method

PotentiodynamicPolarization studies

Figure 4a & 4b show the Tafel polarization curves for mild steel with and without addition of *CFU* and *CFTU* in 2M HCl respectively. The curves from both the compounds showed that, the added inhibitors control both anodic and cathodic reactions and behaves as mixed type of inhibitors [31].

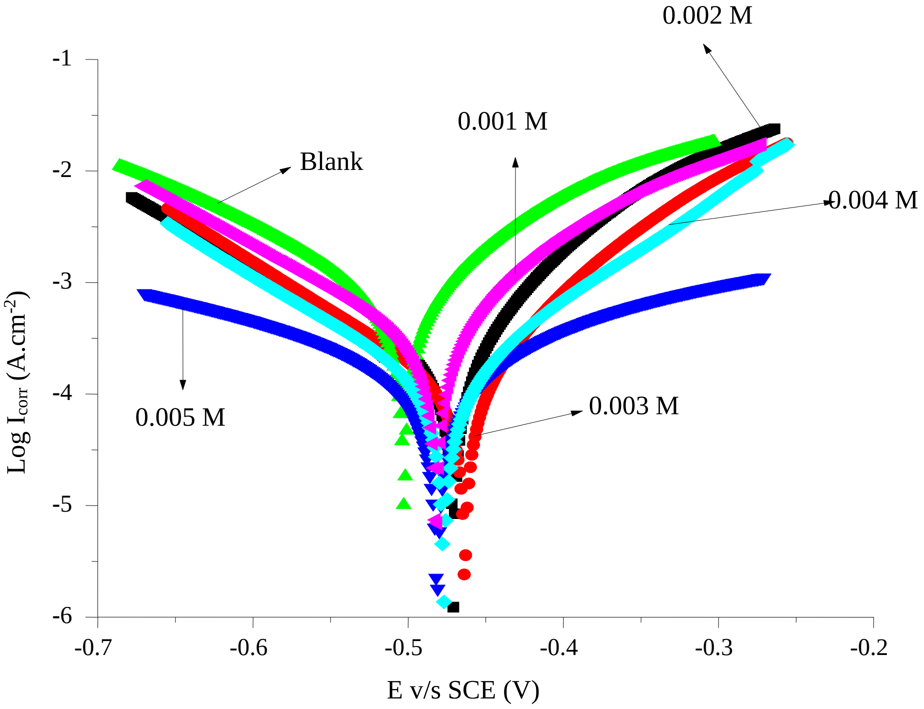


Figure 4a: Tafel plots for mild steel in 2M HCl in presence of different concentration of *CFU* at 301 ± 1K.

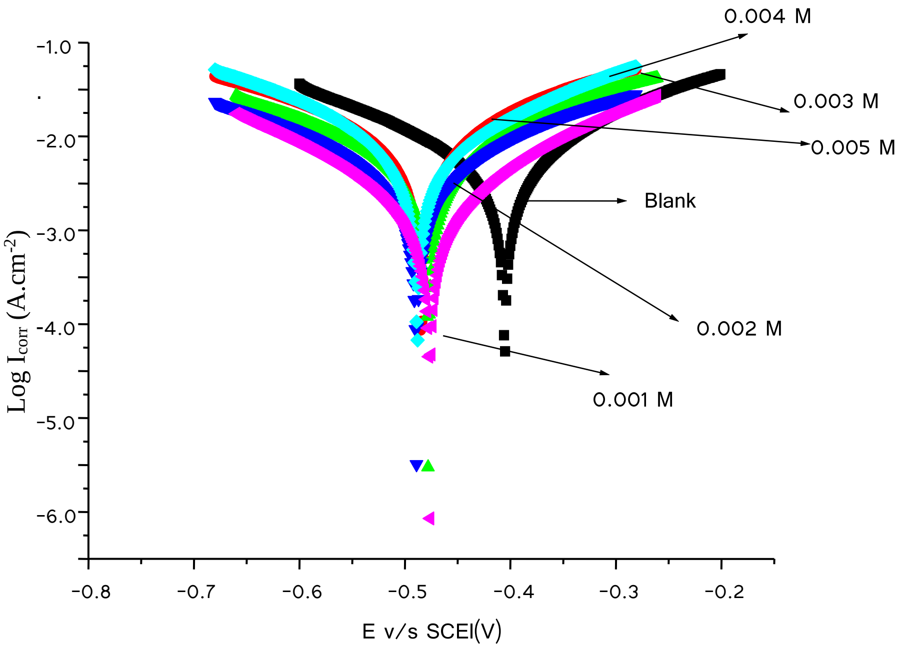


Figure 4b: Tafel plots for mild steel in 2M HCl in presence of different concentration of *CFTU* at 301 ± 1K.

The various parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic (β_a) and cathodic (β_c) Tafel slopes, and percentage inhibition efficiency (%IE) obtained from the polarization measurements are reported in Table 5. The results showed that the addition of the inhibitors to the acid solution influenced both the anodic and cathodic half-cell reactions by shifting the anodic and cathodic potentials towards lower values of corrosion current density. This type of shifting of electrode potentials is due to the development of organometallic layer on metal surface and control the rate of electron transfer at the metal-electrolyte interface. Hence the reduction reaction would controlled by charge transfer process [32, 33].

Table 5: Corrosion parameters obtained from polarization measurements for mild steel in 2M HCl containing various conc. of *CFU* and *CFTU* at 301 ± 1 K.

Inh. Conc. [M]	**E_{corr} (V)**	**I_{corr} (A cm^{-2})**	**β_c mV/decade**	**β_a mV/decade**	**%IE**
Blank	-0.418	0.170	-220	160	----
			CFU		
0.001	-0.496	0.102	-170	130	40.00
0.002	-0.486	0.078	-150	110	54.11
0.003	-0.479	0.052	-120	120	69.41
0.004	-0.474	0.040	-220	250	76.47
0.005	-0.470	0.028	-110	140	83.52
			CFTU		
Blank	-0.668	0.182	-220	160	-
0.001	-0.663	0.098	-170	130	46.15
0.002	-0.657	0.056	-150	110	69.24
0.003	-0.658	0.040	-120	120	78.02
0.004	-0.653	0.030	-220	250	83.51
0.005	-0.650	0.028	-110	140	88.42

3.5. Nature of adsorption isotherm

The corrosion of mild steel is controlled in the presence of inhibitor is due to the adsorption of the inhibitor molecules on mild steel surface. Figure 5 describes the plots of log (θ/1-θ) v/s log (C) for adsorption of *CFU* & *CFTU* on mild steel in 2M HCl respectively. The plots gave straight line, it revealed that the adsorption process fit to the Langmuir's adsorption isotherm. The strong correlation of regression coefficients of the fitted curves are (R^2= 0.9743 and 0.8988) of the Langmuir adsorption isotherm for *CFU* and *CFTU* was observed. This reveals that the inhibition tendency of the inhibitors is due to the adsorption of these molecules on the metal surface.

*3.6***.** *Thermodynamic parameters*.

The dependence of the adsorption constant (K_{ads}) on standard free energy of adsorption (ΔG_{ads}) can be followed by the equations (8) & (9). The values of K_{ads} and ΔG_{ads} in 2M HCl solution containing optimised concentration of *CFU* & *CFTU* were calculated and presented in Table 6. Results showed that the high value K_{ads} signifies the high adoptability of the inhibitors on metal surface. The increase in solution temperature results into decrease in K_{ads} values. The values of ΔG_{ads} either equal or greater than -20 kJ mol^{-1} resulted into physisorption between charged inhibitor and metallic surfaces. It is manifested that in acidic solution inhibitors having heteroatoms exist in their cationic forms due to their protonation and metallic surfaces become anionic due to adsorption of counter ions of aggressive acidic solutions thereby a physisorption occur between oppositively charged species. The values of ΔG_{ads} in the present study for studied inhibitors are more than -20 kJ mol^{-1} which argue that the inhibitors adsorbed by physisorption mechanism. Further the negative values of ΔG_{ads} were revealed that, the inhibitor molecules adsorbed spontaneously on mild steel surface and control the corrosion to a greater extent.

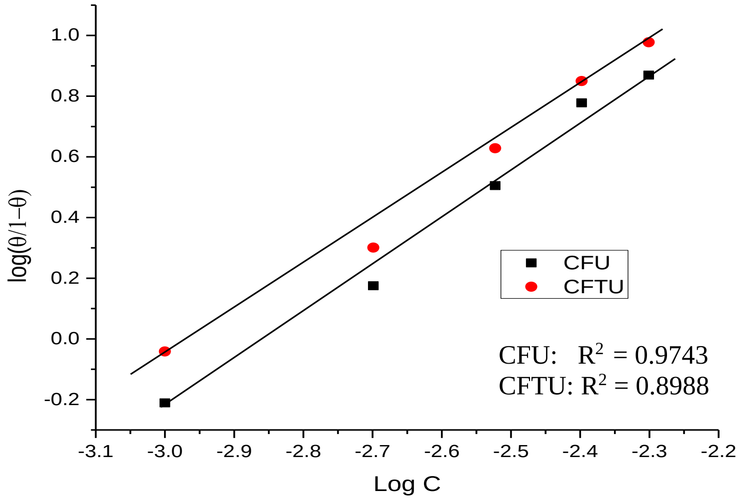


Figure 5: Langmuir adsorption isotherm for mild steel in presence of CFU & CFTU in 2M HCl at 301 ± 1 K

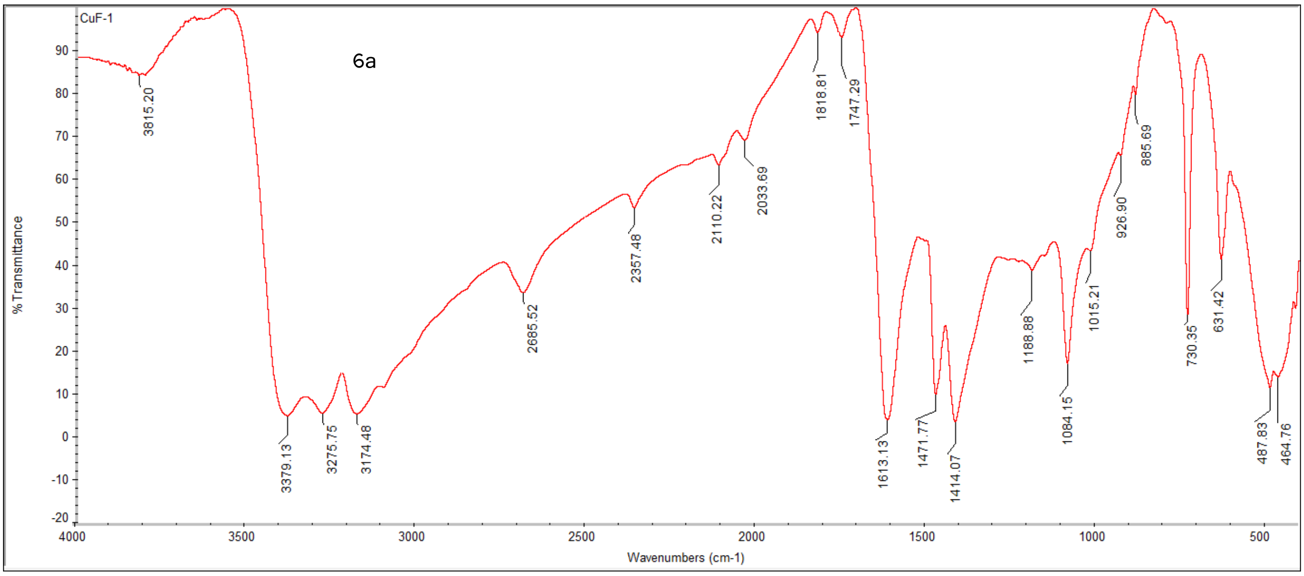
Table 6: Thermodynamic parameters derived for *CFU* & *CFTU* at studied temperatures.

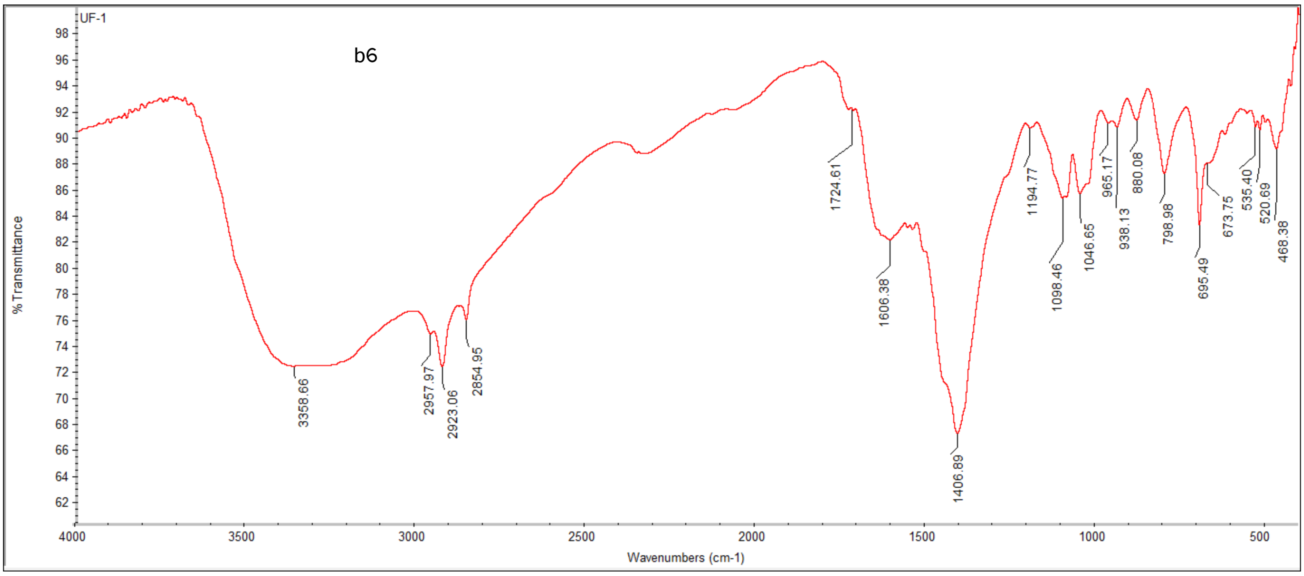
Temp. [K]	**K_{ads} (M^{-1}) (CFU)**	**K_{ads} (M^{-1}) (CFTU)**	**$-\Delta G^o_{ads}$ kJ mol^{-1} (CFU)**	**$-\Delta G^o_{ads}$ kJ mol^{-1} (CFTU)**
301	1199	1549	27.79	28.43
311	600	741	26.93	27.47
321	462	506	26.09	27.34

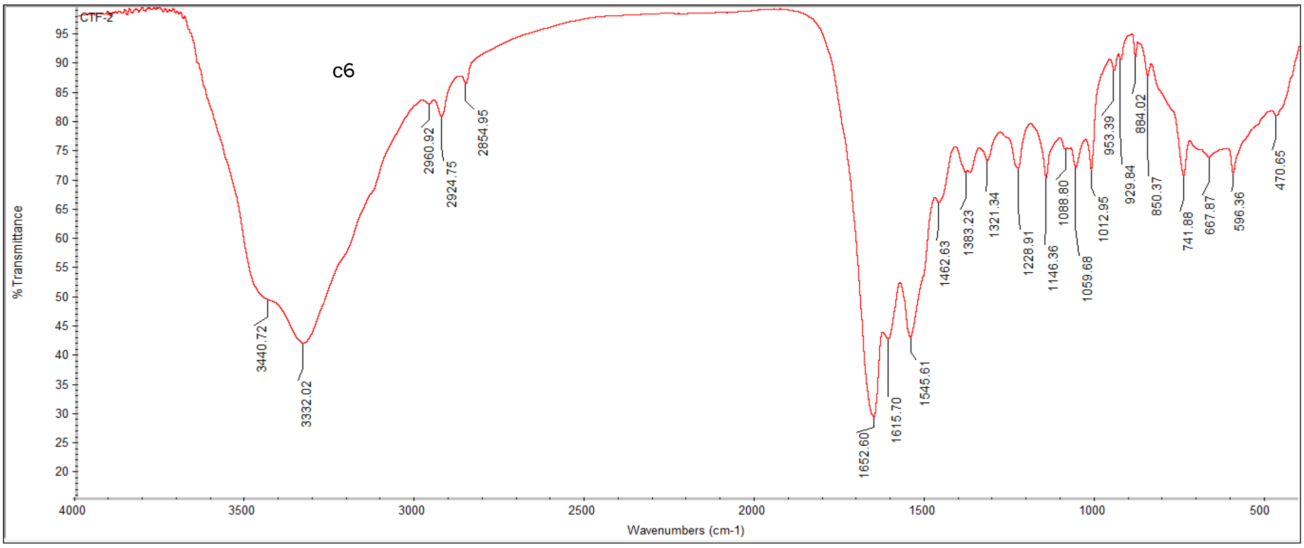
3.7. Surface characterization

Fourier Transform Infrared Spectroscopic studies (FTIR)

FTIR investigations were made to know the possible interactions between the adsorbed inhibitor on mild steel surface in acid solution. Figure 6a shows the FTIR spectrum of the pure *CFU* compound and Figure 6b is that of spectrum of the scratched compound from the corroded mild steel surface in 2M HCl containing optimized concentration of the *CFU* inhibitor. Similarly Figure 6c & 6d are the FTIR spectra of the pure *CFTU* and scratched compound of *CFTU* respectively. In Figure 6a, the characteristic stretching bands at 1613.13 cm^{-1}, 1747.29 cm^{-1} and 1471.17 – 1414.07 cm^{-1} are indicated -C=N, C=O and C-O groups respectively. In Figure 6b the characteristic stretching bands are slightly varied and appeared at 1606.38 cm^{-1}, 1724.61cm^{-1} and 1406.89 cm^{-1} corresponds to -C=N, C=O and C-O groups respectively. Similarly in Figure 6c, the characteristic stretching bands appeared at 1652-1545.61 cm^{-1}, 1088.80-1059.68 cm^{-1} and 1462.63 cm^{-1} are corresponds to -C=N, C=S and C-O groups respectively. The characteristic stretching bands in Figure 6d are slightly altered and appeared at 1653.97-1540.98 cm^{-1}, 1084.74-1020.10 cm^{-1} and 1406.77 cm^{-1} are corresponds to -C=N, C=S and C-O groups respectively. These alteration of the corresponding peaks from the pure compounds to the scratched compounds indicated interaction of the inhibitor molecules on the mild steel surface in presence of HCl medium. Further in the spectrum of *CFU* compound (Figure 6a) at the domains 3379.13 to 3174.48 cm^{-1} peaks are related to C-H stretching vibrations in aromatic ring are modified / disappeared in the spectra of scratched compound of *CFU* (Figure 6b). Similarly, in the spectra of *CFTU* (Fig. 6c) the domains at 3332.02 cm^{-1} peaks are related to C-H stretching vibrations in aromatic ring are modified/disappeared in the spectra of scratched compound of *CFTU* (Fig. 6d). Such modifications/alteration of the peaks revealed that the inhibitor molecules are chemically interacted on mild steel surface and control the corrosion of mild steel in acid medium [36].







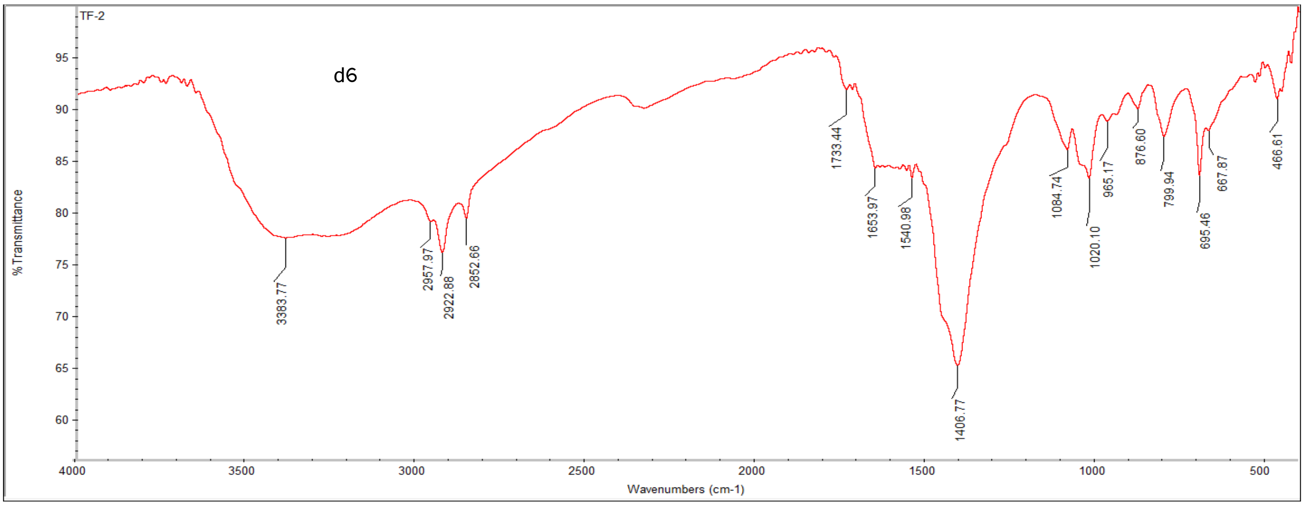


Figure 6: FTIR Spectra of : a) pure *CFU*, b) scratched *CFU* from the corroded mild steel surface, c) pure *CFTU*, d) scratched *CFTU* from the corroded mild steel surface

Scanning Electronic Microscopic studies (SEM)

The change of surface morphology of mild steel during corrosion and corrosion inhibition process was studied by scanning electron microscope (SEM: Model-JEOL make, JSM-IT 500LA). Figure 7a shows the SEM images of polished untreated mild steel surface it shows the heterogeneous nature of the metal surfaces.

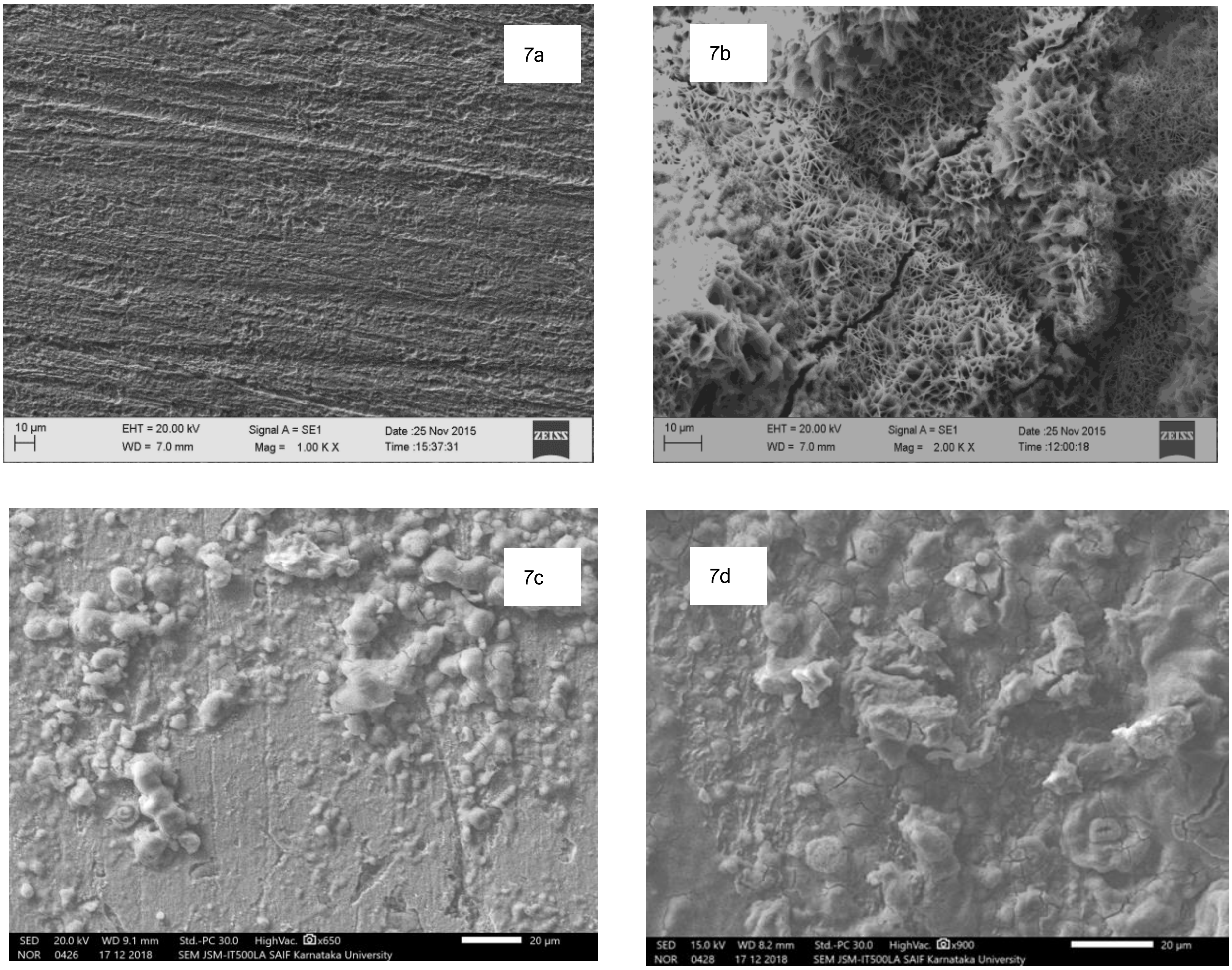


Figure: 7a SEM image of polished mild steel surface, **7b** Corroded mild steel surface in 2M HCl immered in 1hour ; **7c** Corroded mild steel surface in 2M HCl containing *CFU* and 7**d** Corroded mild steel surface in 2M HCl containing *CFTU*

Figure 7b shows the corroded mild steel surface for 1hour in 2M HCl at 301 ± 1 K. The surface contained large number of small cavities and covered with grooves of needle shaped corrosion products. In addition to this cracking of the corrosion products layer loosely adherent to the surface. Due to the presence of large number cavities, porous and loosely adherent layer, the dissolution of mild steel in acid solution is more.

Figure 7c and 7d shows the SEM images of corroded mild steel surface in presence of 0.004M *CFU&CFTU* solution respectively. The images shows that, the surface was covered by the film and there is a formation of strong and adherent film and exhibited more corrosion resistant. Further the surfaces shows that, the partial depletion of the film, it suggests that in presence of inhibitor on mild steel surface exhibited higher corrosion resistance in acid solution. In case of Figure 7c the surface was covered less extent and shows less %IE compare to the Figure 7d, which covered more surface area and exhibited higher %IE due to the presence of sulphur atom in the compound [37].

Conclusion

The investigation of corrosion inhibition properties of *CFU* and *CFTU* on mild steel in hydrochloric acid solution was carried out by weightloss and polarization methods. The results show that both the compounds possessed good mild steel corrosion inhibition properties in hydrochloric acid medium. The results reported from weight loss and polarization methods are in good agreement with each other. The percentage inhibition efficiency of the inhibitors depends on the inhibitor concentration, temperature of the medium and molecular structure of the compound. The polarization method revealed that, both the compounds control anodic & cathodic reactions and acts as mixed type inhibitors. The corrosion control takes place via adsorption process and obeys Langmuir's adsorption isotherm.

The adsorption and interaction of the *CFU&CFTU* molecules on mild steel surface was confirmed by FT-IR technique. The inhibitors chemically interacted through heteroatoms with the metal surface and form an organometallic layer. This layer acts as a barrier between the metal – solution interface and reduce the rate of corrosion of mild steel in acid medium. The SEM images indicated that, the *CFU* and *CFTU* compound adsorbed on the mild steel surface and formed a strong thin film, this film resists the corrosion of mild steel surface in aid solution. The percentage inhibition efficiency was found to be greater in case *CFTU* than *CFU* due to the presence of sulphur atom in the functional, which strongly interact on the metal surface and increase the percentage inhibition efficiency of CFTU. Both the studied compounds are water soluble and effectively used as corrosion inhibitors for mild steel in hydrochloric acid medium.

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