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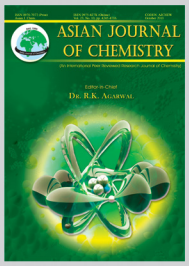

# Effect of Clopidogrel on Corrosion Inhibition of Mild Steel in 1 M $H_2SO_4$

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The inhibitive action of pharmaceutically active clopidogrel on corrosion of mild steel in 1M $H_2SO_4$ was investigated by using weight loss, corrosion potential, potentiodynamic polarization and surface analytical techniques. The change in electrochemical parameters observed by variation on inhibitor concentration within the range of 10-500 ppm favours its adsorption. The compound influences the anodic dissolution of mild steel as well as hydrogen evolution reaction in 1M $H_2SO_4$. Morphology of the mild steel specimens was examined using scanning electron microscopy in presence and absence of inhibitor. The inhibition was due to adsorption of inhibitor molecule on metal surface. Mechanism of adsorption of clopidogrel on the surface of mild steel is proposed for its inhibition behaviour. The adsorption characteristics of the inhibitor were approximated by Langmuir adsorption isotherm. An adherent layer of inhibitor on mild steel surface acted as barrier between metal and aggressive solution.

**Key Words: Mild steel, Inhibitors, Adsorption, Electrochemical techniques, Scanning electron microscopy.**

## INTRODUCTION

Mild steel is choice of material of construction in most of the chemical industries. Corrosion of mild steel is a significant concern for the chemical processing industry. Corrosion failure can disrupt production or cause unintended release of chemicals into the environment. Sulphuric acid is widely used in chemical as well as petrochemical industries for acid pickling, acid descaling, industrial cleaning, petrochemical processes and chemical process development. During the course of pickling, there is the danger that metal dissolution from already cleaned metal surface will occur after the removal of the oxides, scale or other coatings. This involves the loss of metal as well as more acid consumption. The mild steel corrosion also involves formation of nascent hydrogen which gets dissolved in metal in atomic form. That gives rise to decrease in the ductility of metal known as pickling brittleness. Inhibitors are added to the acid to prevent these disadvantages associated with a metal corrosion in pickling[1]. Organic molecules are used to inhibit mild steel corrosion in acid solutions[2-11].

The corrosion inhibition of metal may involve either physisorption or chemisorption of the inhibitors to the metal surface and subsequent interference with either cathodic or anodic or both reactions occurring at the adsorption sites. The electrostatic attraction between the charged hydrophilic groups and the charge active centres on the metal surface leads to physisorption. The existing data show that most of the organic inhibitors are adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier film[12]. Organic compounds containing heteroatom such as nitrogen, sulfur, phosphorous, oxygen etc. and aromatic ring, heterocyclic ring, double bond, triple bond in their structure serves as good corrosion inhibitors of metals with great effectiveness especially in aggressive acidic environment[13-15]. Compounds containing more than one heteroatom like nitrogen and sulfur in their structure serves as excellent corrosion inhibitor than those containing nitrogen or sulfur alone[16]. Availability of non-bonded (lone pair) and *p*-electrons in alkenes, alkynes and aromatic rings in inhibitor molecules may involve in chemisorption. The strength of the coordinate covalent bond thus formed depends upon the electron density and polarizability of the donor atom of the functional group[17]. Chemical adsorption has a free energy of adsorption and activation energy higher than physical adsorption and, hence, usually it is irreversible. In case of alkynes it has been proposed that the alkynes undergoes polymerization to form a protective film (coating) on the metal surface[18] and the film prevents mass transport and results in inhibition of corrosion[19]. Some researcher groups have investigated corrosion inhibition efficiency of naturally occurring materials in acidic media such as natural honey[20,21], henna[22], opuntia extract[23], guar gum[24], jojoba oil[25], artemisia oil[26] and *Telferia occidentalis* extract[27].

The inhibitive capabilities of antifungal drugs clotrimazole and fluconazole on corrosion of aluminum in HCl has been

reported by Obot *et al*.[28]. Some quinoline derivatives have been found effective corrosion inhibitor for mild steel in sulfuric acid[29,30]. Inhibition of steel corrosion in acid solution by pharmaceutically active compounds such as pheniramine, mebendazole[31,32], ketoconazole, cefazolin, doxycycline and diethylcarbamazine[33-35] have been investigated. Rhodanine azosulpha and some antibacterial compounds have been reported by Abdallah[36,37] as efficient corrosion inhibitors in acidic media.

In present study, we intend to find out inhibition property of pharmaceutically active compound clopidogrel towards corrosion of mild steel in 1M sulfuric acid. Surface coverage by clopidogrel over mild steel substrates in corrosive environment was studied using SEM. Possible mechanism of inhibition based on electrochemical and surface analytical studies has been explained.

## EXPERIMENTAL

Mild steel coupons having composition wt % (C- 0.16 %, Si- 0.10 %, Mn-0.40 %, P-0.013 %, S-0.02 % and remaining as iron) have been used as working electrode in the present investigation. For electrochemical polarization and weight loss studies, coupons of 1.0 cm × 3.0 cm × 0.025 cm were sheared from the commercial grade sheet. The surface of mild steel coupons were abraded successively by different grades of metallographic emery papers 1/0, 2/0, 3/0 and 4/0 obtained from Sianor, Switzerland, so as to get the surface free from scratch and other apparent defects. The polished samples were washed with soap solution, rinsed with bi-distilled water, degreased with acetone and finally dried. The surface treatments were carried out immediately before each experiment of corrosion test. The aggressive solution was made of AR grade sulphuric acid obtained from Merck Chemicals. One molar solution of sulfuric acid was prepared with double distilled water. The organic inhibitor clopidogrel was used as received without further purification. The chemical structure of clopidogrel is shown in Fig. 1. The measurements were carried out in aerated non-stirred 1M sulphuric acid solution at concentration range of 10-500 ppm as the corrosion inhibitor.

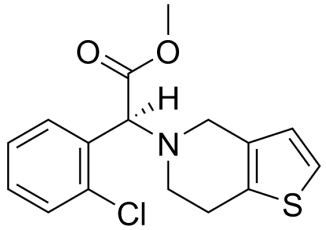



Fig. 1. Chemical structure of clopidogrel

**Weight loss measurements:** Weight loss measurements were carried out in a glass vessel with 100 mL of 1M $H_2SO_4$ solution with and without concentration of inhibitors ranges from 10-500 ppm. The immersion time for weight loss was 24 h at 30 ± 1 ºC. After immersion the coupons were withdrawn, rinsed with double distilled water, washed with acetone, dried and weighed. The experiment was carried out in duplicate and the average value of weight loss was noted.

**Electrochemical measurements:** Electrochemical measurements were carried out on the steady state open circuit potential (OCP). The variation of corrosion potential of mild steel in 1M $H_2SO_4$ was measured against saturated calomel electrode in absence and presence of various concentrations of inhibitors. The time dependence of open circuit potential for different experiments was recorded for 2 h exposure period. Then same sample was used for potentiodynamic polarization (PD) experiments. Potential was swept between -0.5 to +0.5 V at the scan rate of 5 mV/s. Different electrochemical results obtained from potentiodynamic polarization are reported in Table-2. The polarization studies were carried out in unstirred solutions. For electrochemical polarization studies (corrosion potential and potentiodynamic polarization) flag shaped specimens with sufficiently long tail were cut from the mild steel sheet. These samples were polished as described earlier leaving a working area of 1 $cm^2$ on both sides of the flag and a small portion at the tip for providing electrical contact. Rest of the surface was coated with enamel lacquer including side edges. The test specimen was connected to the working electrode holder through the tip of the tail. About 50 mL of the corrosive medium was taken in a mini corrosion testing electrochemical cell. This volume was appropriate to permit desired immersion of electrodes.

Electrochemical measurement system, DC 105, containing software of DC corrosion techniques from M/S Gamry Instruments Inc., (No. 23-25) 734, Louis Drive, Warminster, PA-18974, USA has been used for performing corrosion potential and polarization experiments. The electrochemical studies were performed in a three electrodes Pyrex glass vessel with mild steel coupon as working electrode, saturated calomel electrode as reference electrode and spectroscopic grade graphite rod as counter electrode.

**Scanning electron microscopic analysis:** The composition and surface morphology of corrosion product on mild steel sample after 24 h immersion in 1M $H_2SO_4$ in the absence and presence of 250 ppm of clopidogrel, was studied by a scanning electron microscopy (SEM). The accelerating voltage for SEM picture was 10.0 KV.

## RESULTS AND DISCUSSION

**Weight loss measurement:** Weight loss data of mild steel in 1M $H_2SO_4$ in the absence and presence of various concentrations of inhibitor were obtained and are given in Table-1. Inhibition efficiencies (IE %) were calculated according to previous report[38]:

$$(IE\ \%) = \frac{(W_0 - W_{corr})}{W_0} \times 100 \quad (1)$$

where $W_{corr}$ and $W_0$ are the weight loss of mild steel in the presence and absence inhibitor, respectively.

The results show that the inhibition efficiencies increase with increasing inhibitor concentration. The results obtained from the weight loss measurements are in good agreement with those obtained from the electrochemical methods.

**Adsorption isotherm:** The surface coverage values, θ, (defined as θ = IE %/100), increases with increasing inhibitor concentration as a result of adsorption of more inhibitor

TABLE-1
WEIGHT LOSS DATA FOR INHIBITION OF CORROSION OF MILD STEEL EXPOSED TO 1M $H_2SO_4$ WITH DIFFERENT CONCENTRATION CLOPIDOGREL

| Inhibitor | Conc. (ppm) | Weight loss (mg) | Surface coverage (θ) | Inhibition efficiency (E %) |
|---|---|---|---|---|
| Blank | – | 194 | – | – |
| Clopidogel | 10 | 121 | 0.3762 | 37.62 |
| | 30 | 52 | 0.7320 | 73.20 |
| | 50 | 41 | 0.7887 | 78.87 |
| | 100 | 36 | 0.8144 | 81.44 |
| | 250 | 29 | 0.8505 | 85.05 |
| | 500 | 15 | 0.9227 | 92.27 |

molecules on the steel surface (Table-1). If molecular adsorption at the metal/solution interface is the mechanism through which the corrosion inhibition occurs, several adsorption isotherms can be tested. The simplest, being the Langmuir isotherm, is based on the assumption that all adsorption sites are equivalent and that particle binding occurs independently from nearby sites being occupied or not. Under these circumstances, the proportionality between surface coverage θ and bulk concentration C of the adsorbing compound is as follows[39]:

$$KC = \frac{\theta}{(1-\theta)} \quad (2)$$

here K is the equilibrium constant. It is convenient to rearrange the equation, yielding:

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (3)$$

Plot of log (θ/1 – θ) against the log C gave straight lines with the slope of unit (Fig. 2), which indicates that the adsorption of these compounds on the mild steel surface obeys the Langmuir isotherm. Adsorption parameters of clopidogrel are mentioned in Table-2.

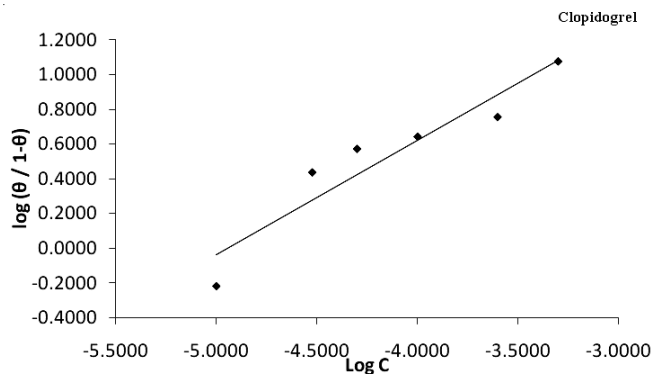



Fig. 2. Adsorption isotherm of clopidogrel

TABLE-2
ADSORPTION PARAMETERS OF CLOPIDOGREL

| C | log C | θ | (1-θ) | θ/(1-θ) | log θ/(1-θ) |
|---|---|---|---|---|---|
| 0.000010 | -5.0000 | 0.3762 | 0.6238 | 0.6031 | -0.2196 |
| 0.000030 | -4.5229 | 0.7320 | 0.2680 | 2.7313 | 0.4364 |
| 0.000050 | -4.3010 | 0.7887 | 0.2113 | 3.7326 | 0.5720 |
| 0.000100 | -4.0000 | 0.8144 | 0.1856 | 4.3879 | 0.6423 |
| 0.000250 | -3.6021 | 0.8505 | 0.1495 | 5.6890 | 0.7550 |
| 0.000500 | -3.3010 | 0.9227 | 0.0773 | 11.9366 | 1.0769 |

**Open circuit potential measurement (OCP):** The electrochemical behaviour of mild steel in 1M $H_2SO_4$ was studied by monitoring change in corrosion potential ($E_{corr.}$) with time. The change in open circuit potential of mild steel in absence and presence of various concentrations of inhibitor clopidogrel in 1M $H_2SO_4$ is shown in Fig. 3.

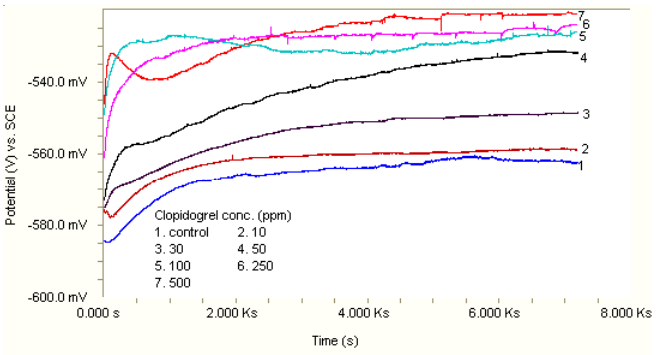



Fig. 3. Corrosion potential of mild steel exposed to 1M $H_2SO_4$ solution with different concentrations of clopidogrel

The change in open circuit potential of mild steel in absence and presence of inhibitors were measured for period of 2 h with sample period of one data per second. The potential attains steady state after exposure of 0.5 h. The steady state potential is an equilibrium state at which $I_{ox.}$ is equal to $I_{red}$. It has been observed that open circuit potential of mild steel from moment of immersion in 1M $H_2SO_4$ tends towards more negative value in absence of inhibitor. This shows corrosiveness of medium which is due to breakdown of pre-immersion, air formed oxide film on the metal surface. In the presence of various concentrations of inhibitors the steady state potential of mild steel shifts more towards positive value. This is due to adsorption of inhibitors on metal surface resulting in passivation of metal.

The influence of various concentration (10, 30, 50, 100, 250 and 500 ppm) of clopidogrel on open circuit potential of mild steel in 1M $H_2SO_4$ is given in Fig. 3. It is obvious from figure that, it exhibit good inhibition performance at 100 ppm and above. Inhibition efficiency increases with increase in concentration of clopidogrel.

**Potentiodynamic polarization measurement:** Fig. 4 depicts typical potentiodynamic polarization curves for mild steel in 1M $H_2SO_4$ solution in the absence and presence of different concentrations of clopidogrel at 30 ºC.

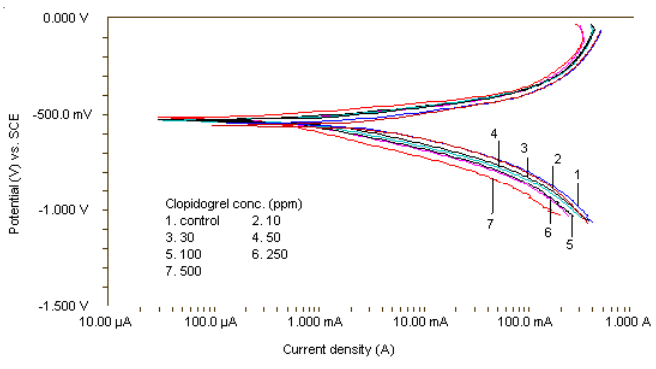



Fig. 4. Potentiodynamic polarization curve of mild steel exposed to 1M $H_2SO_4$ with different concentrations of clopidogrel

The corrosion inhibition efficiency was calculated by using the following equation:

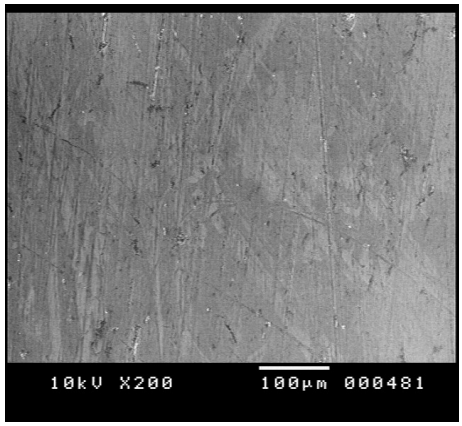
$$\text{Inhibition efficiency (IE \%)} = \frac{100(i_o - i)}{i_o} \quad (4)$$

where $i_o$ and i are the corrosion current densities in the absence and presence of inhibitor in the solution, respectively. Various corrosion parameters such as corrosion potential ($E_{corr}$), anodic and cathodic Tafel slopes (βa, βc), the corrosion current density ($I_{corr}$) and the inhibition efficiency (IE %) are given in Table-3.

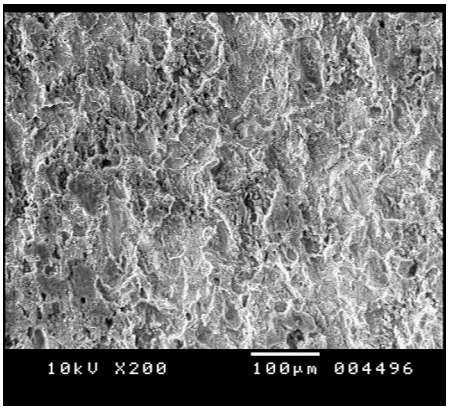
It can be seen from the experimental results derived from polarization curves that in the presence of these compounds $I_{corr}$ decreases significantly at all of the studied concentrations. The presence of clopidogrel resulted in a slight shift of the corrosion potential towards the active direction in comparison to the result obtained in the absence of the inhibitor. Both the anodic and cathodic current densities were decreased indicating clopidogrel suppressed both the anodic and cathodic reactions. This phenomenon may be due to the existence of a phenyl ring having high electron density[40,41]. Clopidogrel shows maximum inhibition efficiency of 93 % at 500 ppm, which may be attributed to the presence of thiophene ring containing sulfur in its structure. The unchanged Tafel slopes βa and βc in the presence of clopidogrel is indicative that the inhibitor acted by merely blocking the reaction sites of the metal surface without changing the anodic and cathodic reaction mechanisms. The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration. In the anodic region, the polarization curves of mild steel show that the addition of clopidogrel decreases current densities in a wide range of potential. These results suggest that clopidogrel act as a mixed-type inhibitor of the corrosion of mild steel in $H_2SO_4$ medium. Similar behaviour has already been reported for other organic compounds[42,43]. The results found from the weight loss are in good agreement with the polarization curves.

**Scanning electron microscopic (SEM) analysis:** SEM micrographs obtained from unexposed and exposed specimen coupons in 1.0M $H_2SO_4$ for 24 h in the absence and presence of 250 ppm clopidogrel which are shown in Fig. 5, respectively. The accelerating voltage for SEM scanning was 10 KV. The results obtained from weight loss and electrochemical measurements were further supported by SEM analysis.

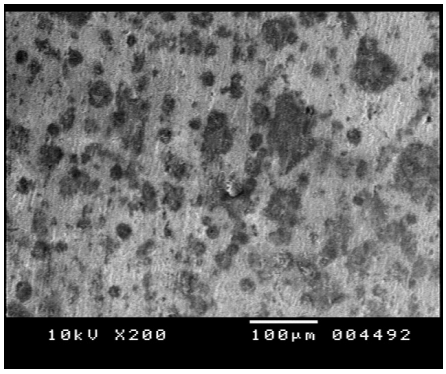
It could be visualized from Fig. 5b that the specimen surface was rougher and was strongly damaged in the absence of the inhibitor. Fig. 5c shows SEM micrograph of the mild steel surface after immersion in 1.0M $H_2SO_4$ containing 250 ppm




(a)




(b)




(c)

Fig. 5. SEM micrographs of mild steel samples (a) unexposed polished mild steel surface (b) after immersion in 1M $H_2SO_4$ solution without inhibitor, (c) after immersion in 1M $H_2SO_4$ solution in presence of 250 ppm of clopidogrel

TABLE-3
ELECTROCHEMICAL PARAMETERS FOR INHIBITION OF CORROSION OF MILD STEEL EXPOSED TO 1M $H_2SO_4$ WITH DIFFERENT CONCENTRATION OF CLOPIDOGREL

| Conc. (ppm) | βa (V/dec.) | βc (V/dec.) | $I_{corr}$ (µA $cm^{-2}$) | $E_{corr}$ (mV) | Corr. rate (mpy) | Inhibition efficiency (%) |
|---|---|---|---|---|---|---|
| Control clopidogrel | 120.5e-3 | 174.7e-3 | 4020 | -555.0 | 1835 | – |
| 10 | 90.0e-3 | 142.1e-3 | 2480.0 | -545.0 | 1134.0 | 38.31 |
| 30 | 77.9e-3 | 132.9e-3 | 1010.0 | -531.0 | 459.4 | 74.88 |
| 50 | 74.3e-3 | 135.0e-3 | 820.0 | -530.0 | 374.9 | 79.60 |
| 100 | 65.6e-3 | 136.9e-3 | 653.0 | -527.0 | 298.5 | 83.76 |
| 250 | 60.7e-3 | 138.4e-3 | 649.0 | -528.0 | 296.4 | 83.86 |
| 500 | 55.9e-3 | 141.3e-3 | 307.0 | -516.0 | 140.1 | 92.63 |

of clopidogrel. It could be observed that extent of damage to mild steel surface is very less, the rate of corrosion was reduced considerably in the presence of inhibitors, it revealed that there was a good protective film adsorbed on metal surface, which acted as a barrier and was responsible for the inhibition of corrosion.

**Mechanism of corrosion inhibition:** Electrochemical and weight loss methods have been employed to study the behaviour of mild steel in acid media, in the presence of clopidogrel. The increase of inhibition efficiency with increasing inhibitor concentration indicated that a higher coverage of inhibitor on the surface was obtained in a solution with higher concentration of inhibitor. The first stage in mechanism of corrosion inhibition in acid media is adsorption of inhibitor molecule on the metal surface[44]. In most inhibition studies, the formation of donor-acceptor surface complexes between *p*-electrons of inhibitor and the vacant *d*-orbital of metal were postulated[45,46]. Since clopidogrel is organic base, addition of an acid to the aqueous solution of clopidogrel will transform neutral molecule in to the respective cations.

The process of adsorption is influenced by the nature and charge of the metal, chemical structure of inhibitor and the type of aggressive electrolyte. The zero charge potential (PZC) is defined as the metal potential measured against the reference electrode under conditions of zero charge on the metal. At the zero charge potential the ionic double layer is absent at the electrode, at the zero charge potential an electrode is best able to adsorb substance dissolved in the electrolyte. The ability of an electrode to adsorb organic molecules is reduced in the presence of potential difference at the ionic double layer. This is because the field pulls in water molecules having high electric constant, dislodging organic molecules from the surface. Thus the adsorption capacity of an electrode is a maximum close to the zero charge potential. The charge of the metal surface can be determined from the potential of zero charge on the correlative scale ($\psi_c$)[47] by the equation:

$$\psi_c = E_{corr} - E_{q=0} \quad (5)$$

where, $E_{q=0}$ is the potential of zero charge. However, value of $E_{corr}$ obtained in $H_2SO_4$ is: -555 mV *versus* SCE. The zero charge potential of iron is - 650 mV *versus* SCE in $H_2SO_4$[48]. Therefore, the values of $\psi_c$ in sulfuric acid are positive and hence, the mild steel surface acquires positive charge. Accordingly, sulphate ions (in $H_2SO_4$ solution) are firstly adsorbed on the metal surface and consequently, the mild steel surface becomes negatively charged. Due to electrostatic attraction, the protonated molecules of these organic compounds are adsorbed (physiosorption) and high inhibition is expected[49]. Clopidogrel molecule is adsorbed on the mild steel surface through unshared pair of electrons present on S-atoms of unsaturated five membered ring, hence, clopidogrel shows higher efficiency in $H_2SO_4$ solution. Besides electrostatic interaction, chemisorption of these compounds is most probable through their planar *p-p* orbitals on the metal surface having vacant *d-p* orbitals. Iron has incomplete *d*-sub shell, therefore acts as an acceptor of electrons. This is verified by the data for its catalytic activity and its affinity towards metal complex formation[50-52]. Instead of this, *d p-d p* bonds are also formed by the overlap of 3*d*-electrons of Fe-atom to vacant 3*d*-orbital of S-atom in case of clopidogrel and hence, clopidogrel molecules are strongly adsorbed on the mild steel surface.

## Conclusion

The results proved that clopidogrel displayed good corrosion inhibition for mild steel in 1M $H_2SO_4$ solution. Clopidogrel works as mixed-type of inhibitor because both cathodic and anodic curves are shifted in positive direction. The percentage inhibition efficiency increases with increasing the concentration of the inhibitor. Adsorption of the inhibitor molecules on mild steel surface obeys the Langmuir adsorption isotherm. SEM examination of mild steel surface showed the presence of protective surface film formed on mild steel surface which inhibits metal dissolution in $H_2SO_4$ and retards hydrogen evolution (mixed-type inhibitor).

## ACKNOWLEDGEMENTS

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