Evaluation of Norfloxacin and Ofloxacin as corrosion inhibitors for mild steel in different acids: Weight Loss Data

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Abstract: The conventional weight loss data was collected to study the corrosion inhibition of mild steel in various acidic solutions (HCl, HNO_3 and H_2SO_4) by Norfloxacin (NOR) and Ofloxacin (OFLO). The acids containing various concentrations of NOR and OFLO were used for weight loss studies at 298 K. The inhibition efficiencies were obtained and interpreted. The inhibition efficiencies increase with increase in inhibitor concentrations. This may be due to the film formed on the surface of the metal due to adsorption of NOR and OFLO that stops access of the corrosive substance to the metal.

Keywords: Corrosion, Mild Steel, Antibiotics, Adsorption, Weight loss data

1. INTRODUCTION

Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment. Mild steel (MS) has many industrial applications because of its easy availability, low cost, uncomplicated fabrication of it into water pipe lines [1-3] etc. Use of inhibitors is an important method in the protection of metal from corrosion. Most of the well-known inhibitors are organic compounds containing nitrogen, sulphur and oxygen. The use of antibiotics and other drugs have been investigated [4-12] and their inhibition efficiencies have been linked with their heterocyclic nature [13-19]. Most of the heterocyclic drugs are environmental friendly. In the present study, the inhibitive properties of antibiotics namely Norfloxacin (NOR) and Ofloxacin (OFLO) on the corrosion of MS in acidic medium are reported using weight loss techniques in various acid solutions at various concentrations.

2. MATERIALS AND METHODS

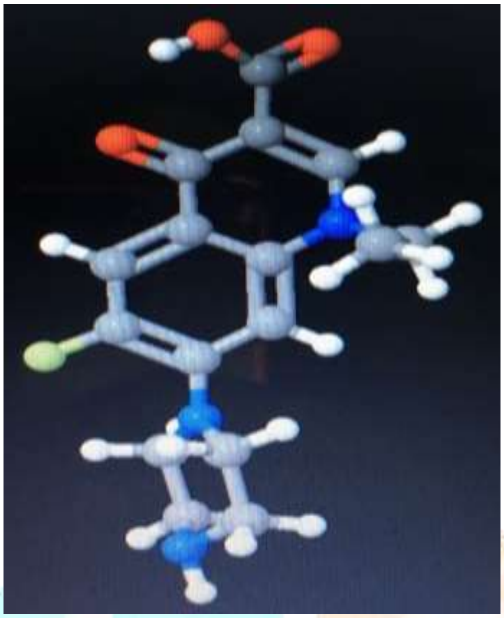
Different acids containing various concentration of NOR and OFLO (500, 700, 900 and 1100 ppm) were used for weight loss studies at 298 K for 6 hours of immersion time .The MS specimen of (1cm x 1cm x1cm) dimensions was smoothened by abrading the surfaces with the help of grinding machine by using 100, 150, 320, 400, 600 and 1000 grade emery papers. They were finally polished by 2000 grade emery paper to a mirror like surface. The specimens were then thoroughly washed with distilled water and finally cleaned with acetone and were dried in a dessicator for 24 hours and finally weighed.

The aggressive solutions were prepared by dilution of analytical grade HCl, HNO_3 and H_2SO_4 obtained from Qualigens Fine Chemicals with doubly distilled water. The chemical composition of MS is given in table 1:

Table 1: The chemical composition of MS

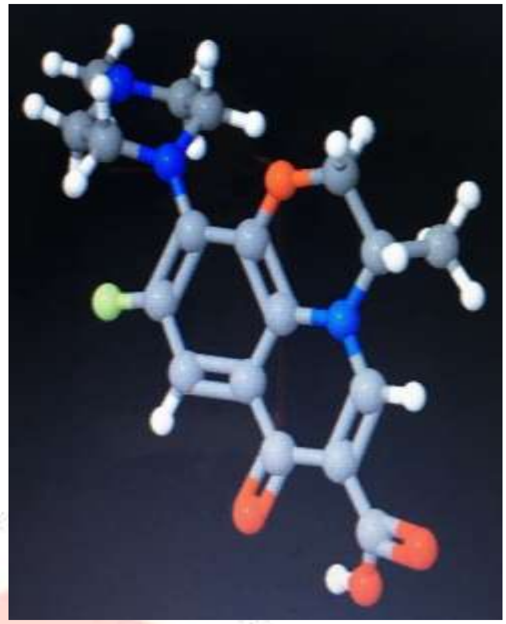
% C	% Si	% Mn	% P	% S	% Cr	% Ni	% Cu	% Fe
0.18	0.19	0.51	0.44	0.057	0.14	0.09	0.06	98.33

NOR and OFLO were obtained from Chemo Chemicals of AR grade. These were used without any further purification for the preparation of different concentration solution (1100, 900,700 and 500 ppm) in various acidic solutions [HCl (1N), HNO_3 (1N) and H_2SO_4 (1N)]. The structures of NOR and OFLO is shown in Fig. 1.



(a) Norfloxacin

1-Ethyl-6-fluoro-1, 4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid



(b) Ofloxacin

(±)-9- fluoro-2,3-dihydro-3-methyl-10- (4-methyl-1-piperazinyl)-7-oxo-7H- pyrido[1,2,3-de]- 1,4-benzoxazine - 6- carboxylic acid

Fig.1. Chemical structure of Norfloxacin and Ofloxacin respectively

The test specimens were dipped in pure acids and various concentrations for both inhibitors. The steel specimens before and after dipping in corrosion solution were weighed and loss in weights were calculated. The percentage of inhibition efficiency IE% was obtained using the formula.

$$IE\% = \frac{(Wo-Wi)}{Wo} \text{ x } 100$$

Where, W_o = weight loss in the uninhibited solution and W_i = weight loss in the inhibited solution of various concentrations

3. Results and Discussion

3.1 Weight loss analysis

The weight loss data of MS in various acid concentrations for different acids at 298K is given in table 2

Table 2: Weight loss data of MS in various concentrations of acids at 298 K

Acid	Concentration (N)	Loss in weight (ΔW)/g	% Loss in weight
HCl	10^{-3}	0.0348	9.67
	10^{-2}	0.0351	9.98
	10-1	0.0379	10.65
	1	0.0385	10.84
H_2SO_4	10^{-3}	0.0398	11.64
	10^{-2}	0.0421	11.89
	10^{-1}	0.0485	13.0
	1	0.0520	13.90
HNO_3	10^{-3}	0.0554	15.40

	10^{-2}	0.0570	15.93
	10^{-1}	0.0590	15.69
	1	0.0621	17.3

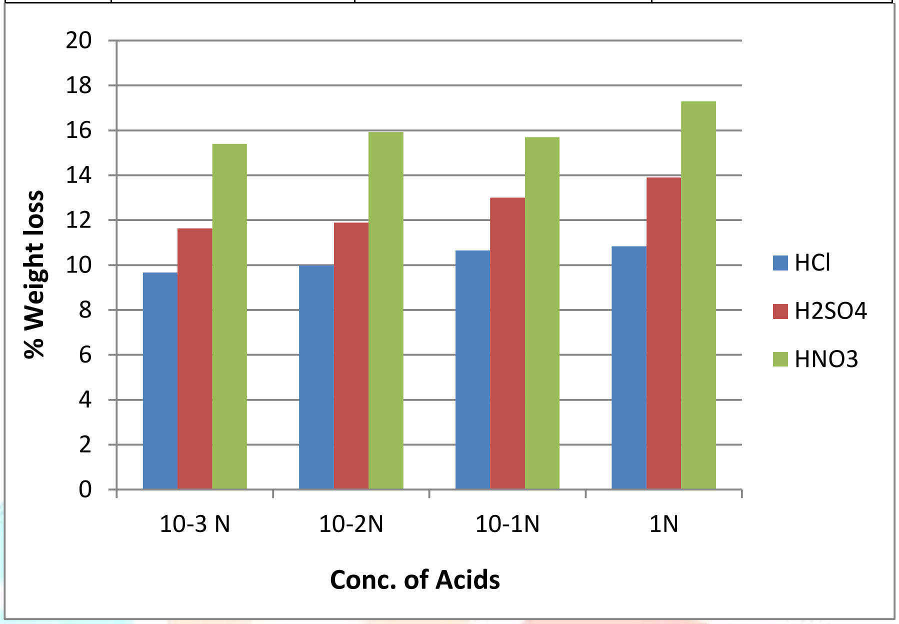


Fig.2: % Weight Loss vs. Conc of various acids at 298K

% Weight loss was found to be maximum for HNO_3 and minimum for HCl. The result is in accordance with the results reported in literature [20-24]. The % weight loss was found to increase with increase in concentrations for all the acids.

The corrosion data of MS in 1N of various acidic solutions (HCl, HNO_3 and H_2SO_4) in the presence of NOR and OFLO are shown in the Tables 3-5.

Table 3: Corrosion data of MS in 1N HCl in the presence of various concentrations of NOR and OFLO

Compound	Concentration(ppm)	Loss in weight (ΔW)/g	% Loss in weight	IE%
	0	0.0379	10.65	
NOR	500	0.0068	1.83	82.15
	700	0.0038	1.17	89.90
	900	0.0052	1.52	86.29
	1100	0.0032	0.88	91.54
	0	0.0370	10.40	
OFLO	500	0.0062	1.77	83.21
	700	0.0051	1.41	86.09
	900	0.0042	1.13	88.76
	1100	0.0029	0.79	92.13

From table 3, it can be concluded that efficiencies of both NOR and OFLO increase with increase in concentration of the inhibitor. The efficiency of NOR at 1100 ppm is found to be 91.5 % whereas for OFLO at the same concentration it was found to be 92.1%. OFLO seems to be slightly efficient inhibitor for the corrosion of MS in 1N HCl. Both the inhibitors show good inhibition efficiencies at lowest studied concentration also (500 ppm).

Table 4: Corrosion Parameters of MS in 1N H_2SO_4 solution in the presence of various concentrations of NOR and OFLO

Compound	Concentration(ppm)	Loss in weight (ΔW)/g	% Loss in Weight	IE%
	0	0.0520	13.90	
NOR	500	0.0063	1.77	87.89
	700	0.0051	1.39	90.14
	900	0.0045	1.23	91.41
	1100	0.0026	0.68	94.98
	0	0.0402	11.89	
OFLO	500	0.0063	1.75	84.39
	700	0.0037	1.09	90.85
	900	0.0029	0.80	92.69
	1100	0.0020	0.56	95.02

Table 4 shows that the efficiencies of both NOR and OFLO increase with increase in concentration of the inhibitor. The efficiency of NOR at 1100 ppm is found to be 94.9 % whereas for OFLO at the same concentration it was found to be 95.0%. OFLO seems to be at par in inhibiting the corrosion of MS in 1N H_2SO_4 except at 500 ppm where the trend is reversed. Both the inhibitors show good inhibition efficiencies at lowest studied concentration also (500 ppm).

Table 5: Corrosion Parameters of MS in 1N HNO_3 solution in the presence of various concentrations of NOR and OFLO

Compound	Concentration(ppm)	Loss in weight (ΔW)/g	% Loss in weight	IE%
	0	0.0621	17.3	
NOR	500	0.0250	7.06	59.9
	700	0.0212	5.94	65.78
	900	0.0119	3.2	80.90
	1100	0.0092	2.5	85.15
	0	0.0599	17.22	
OFLO	500	0.0306	8.5	48.97
	700	0.0216	5.74	63.87
	900	0.0112	3.14	81.25
	1100	0.0083	2.34	86.16

Table 5 indicates that efficiencies of both NOR and OFLO increase with increase in concentration of the inhibitor. The efficiency of NOR at 1100 ppm is found to be 85.2 % whereas for OFLO at the same concentration it was found to be 86.2 %. OFLO has an edge over NOR in inhibiting the corrosion MS in 1N HNO_3 till 900 ppm whereas at 700 ppm and below the trend is reversed.

OFLO shows the best efficiency in inhibiting corrosion of MS in 1N H_2SO_4, followed by 1N HCl and least in 1N HNO_3. NOR follows the similar trend in these three acids (1N) .Overall it can be said that both the inhibitors follow the trend of decreasing efficiency at different acids as follows:

$$H_2SO_4 > HCl > HNO_3$$

OFLO is found to be slightly better inhibitor in combating corrosion as compare to NOR. The reason may be attributed to the planarity of the phenyl rings, more number of heteroatoms and higher molar mass (Fig. 1)

3.2 Adsorption Isotherm

Various adsorption isotherms for NOR and OFLO in acids were plotted, their slope and correlation coefficient values are reported in table 6 and 7 respectively. In order to obtain the adsorption isotherm, the degree of surface coverage (Ɵ) was calculated using:

$$\theta = \frac{IE\%}{100}$$

Where Ɵ is the surface coverage and IE% is the inhibition efficiency.

Table 6: Slope and correlation coefficient values for different adsorption isotherms for NOR in different acids

Acid	Adsorption Isotherm	Slope	R^2
1N HCl	Langmuir	1.021	0.990
	Freundlich	0.111	0.621
	Temkin	0.221	0.616
	El-Awady	0.857	0.597
	Flory-Huggins	0.65	0.497
	Frumkin	1.136	0.198
1N H_2SO_4	Langmuir	0.988	0.998
	Freundlich	0.091	0.932
	Temkin	0.192	0.925
	El-Awady	1.107	0.854
	Flory-Huggins	0.748	0.826
	Frumkin	13.32	0.639
1N HNO_3	Langmuir	0.711	0.947
	Freundlich	0.477	0.948
	Temkin	0.787	0.940
	El-Awady	1.803	0.931
	Flory-Huggins	0.342	0.786
	Frumkin	0.821	0.905

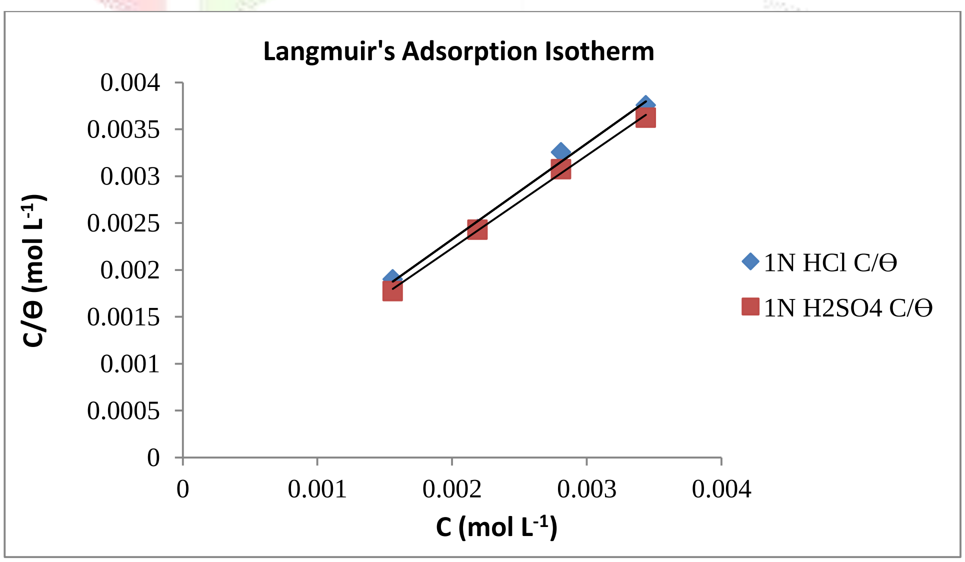


Fig.3: Langmuir adsorption isotherm for NOR in 1N HCl and 1N H_2SO_4 on MS

The plot of C/Ө versus C is linear as shown in Fig.3. indicating that the adsorption NOR in 1N HCl and H_2SO_4 on the MS surface is consistent with Langmuir isotherm and the slopes obtained are unity. The Langmuir isotherm equation is expressed as:

$$\frac{C}{\theta} = \frac{1}{K} + C$$

Where, K is the equilibrium constant for the adsorption process, Ө is the degree of surface coverage and C is molar concentration of inhibitor used in the corrosive solution. As the adsorption isotherm is of Langmuir type, monolayer of the inhibitor species must have been attached to the MS surface with uniformity of its surface and no lateral interaction between the adsorbed species.

Fig.4 revealed Freundlich adsorption isotherm for NOR in 1N HNO_3 on the MS surface and is given by the equation [25].

$$\text{Log } \Theta = \log K + \frac{1}{n} \log C$$

Where $\frac{1}{n}$ is heterogeneity parameter. The value of $\frac{1}{n}$ is used to describe the ease of adsorption. Usually, when $0 < \frac{1}{n} < 1$, adsorption is believed to be easy, and moderate or difficult when $\frac{1}{n} = 1$ or $\frac{1}{n} > 1$ respectively [26]. The smaller $\frac{1}{n}$, the greater the expected heterogeneity. If n lies between 1-10, this indicates a favorable adsorption process [27] .From the graph, the value of $\frac{1}{n}$ is 0.477 while n = 2.0964 indicating that the adsorption of NOR on MS (1N HNO_3) is favorable and the R^2 value is 0.948.

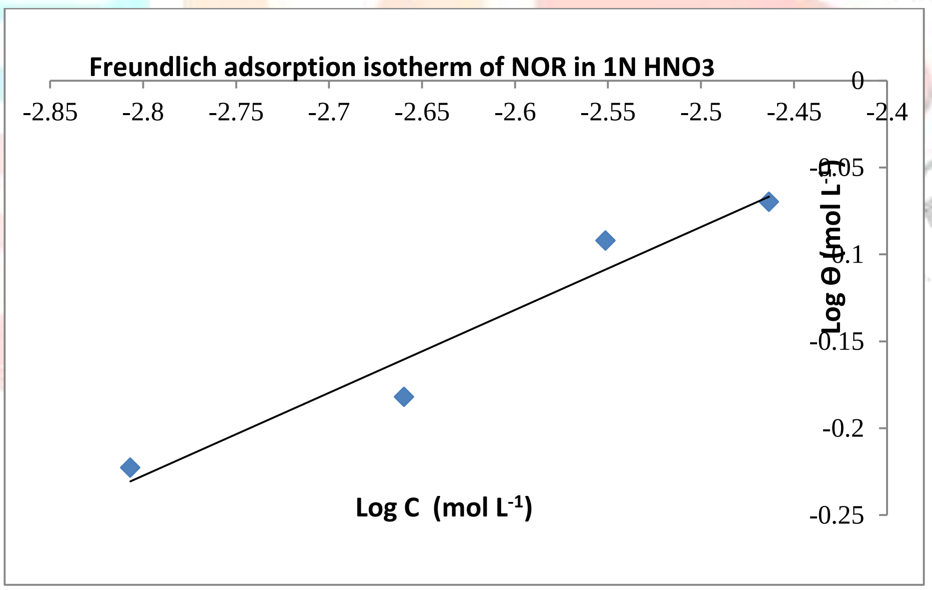


Fig.4: Freundlich adsorption isotherm of NOR in 1N HNO_3 on MS

Table 7: Slope and correlation coefficient values for different adsorption isotherms for OFLO in different acids

Acid	Adsorption Isotherm	Slope	R^2
1N HCl	Langmuir	0.99	0.998
	Freundlich	0.126	0.981
	Temkin	0.254	0.976
	El-Awady	1.048	0.937
	Flory-Huggins	0.876	0.919
	Frumkin	0.346	0.105
1N H_2SO_4	Langmuir	0.947	0.999

	Freundlich	0.146	0.954
	Temkin	0.302	0.960
	El-Awady	1.541	0.986
	Flory-Huggins	0.602	0.981
	Frumkin	1.789	0.939
1N HNO_3	Langmuir	0.363	0.836
	Freundlich	0.769	0.976
	Temkin	1.163	0.981
	El-Awady	2.513	0.982
	Flory-Huggins	0.127	0.756
	Frumkin	1.307	0.980

It is evident from the R^2 values that the adsorption of OFLO in 1N HCl and H_2SO_4 follows Langmuir adsorption isotherm (Fig 6) indicating monolayer adsorption of OFLO on the MS surface as explained earlier.
OFLO follows El-Awady adsorption isotherm in 1N HNO_3.The graph for adsorption of OFLO is shown in Fig.6.
The El-Awady isotherm is represented as:

$$\text{Log}\left(\frac{\theta}{1-\theta}\right) = \log K' + y \log C$$

Where K' is the equilibrium constant for the adsorption and $K = K'^{1/y}$, here y represents the number of water molecules replaced by one inhibitor molecule. The value of 1/y less than unity suggests multilayer adsorption whereas the value greater than unity indicates that the inhibitor occupies more than one active sites [28-29].

The lower 1/y value (0.3979) suggests the multilayer adsorption of OFLO on MS surface in 1N HNO_3.

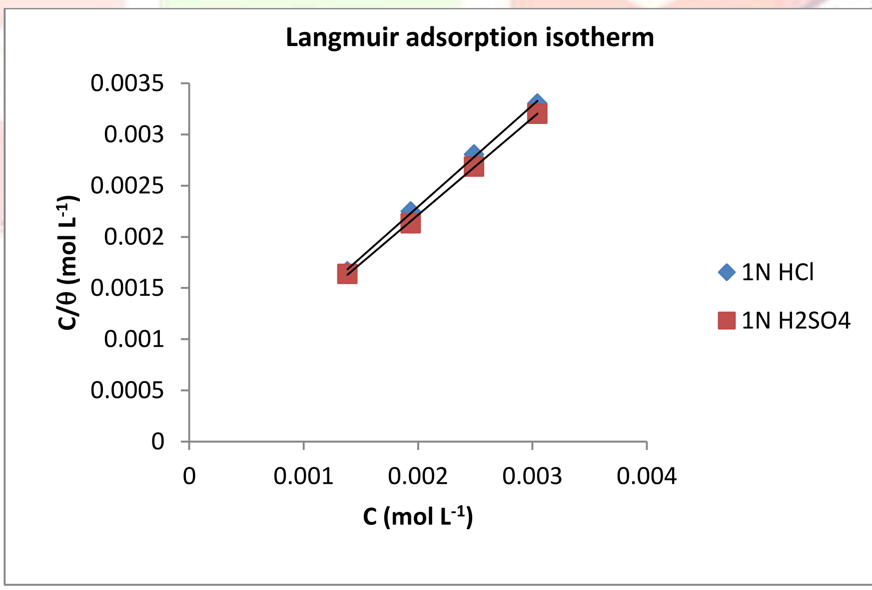


Fig.5: Langmuir adsorption isotherm of OFLO in 1N HCl and 1N H_2SO_4 on MS

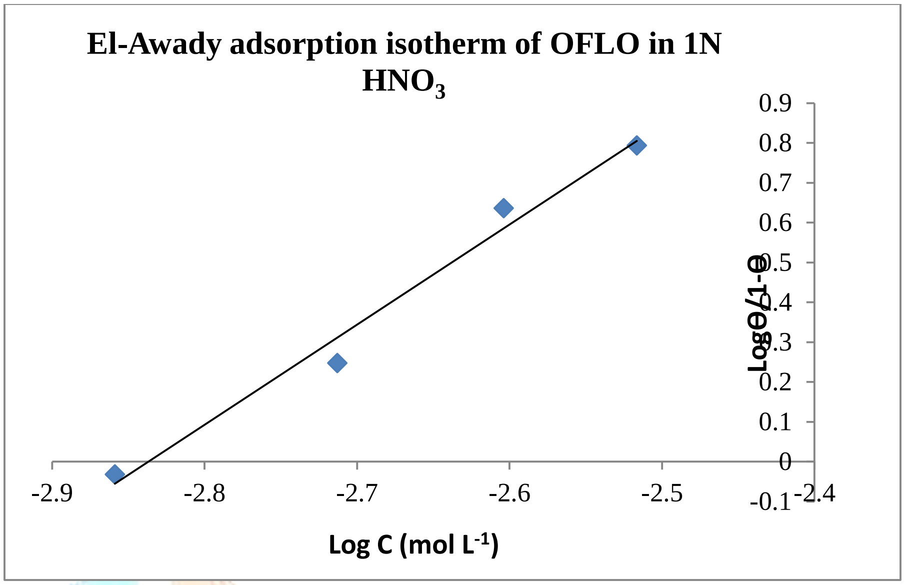


Fig.6: El-Awady adsorption isotherm of OFLO in 1N HNO_3 on MS

Antibiotics studied (NOR & OFLO) have high molar mass and these molecule are able to cover large surface area of the metal. The adsorption mechanism seems to be through the hetero atoms (N, O, and F) and the aromatic ring interacting with the empty d-orbital of the metal surface. There may also be possible electrostatic interaction between negatively charged metal surface and the protonated inhibitor molecule. To further confirm the mechanism of adsorption process it is proposed to carry out temperature kinetics, surface morphology and quantum chemical studies.

4. Conclusion

1. The weight loss data shows that both the antibiotics NOR and OFLO inhibit the corrosion of MS in acidic medium (HCl , H_2SO_4 and HNO_3)
2. The inhibition efficiency was found to increase with increase in concentration of both the inhibitors in all the acids.
3. For all the three acids the inhibition efficiencies show the order: OFLO > NOR.
4. The inhibitors NOR and OFLO adsorb on the metal surface according to Langmuir adsorption isotherm in 1N HCl and H_2SO_4 thereby suggesting monolayer formation.
5. NOR and OFLO adsorb on MS in 1N HNO_3 as per Freundlich and El-Awady adsorption isotherms respectively.
6. The inhibition shows the trend H_2SO_4 > HCl > HNO_3.

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