



## Potential of Expired Ofloxacin as Corrosion Inhibitor of Mild Steel in 1M HCl Solution

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### ABSTRACT

The Potential of expired ofloxacin as an inhibitor of mild steel corrosion in 1 M HCl solution was investigated using gravimetric mass loss (weight loss) and electrochemical (linear polarization) methods. The investigations were carried out at temperatures of 30 and 50 °C and inhibitor concentrations ranging from 100 to 500 ppm. Results obtained revealed an increase in inhibition efficiency with an increase in the concentration of the inhibitor (expired ofloxacin) and a decrease in inhibition efficiency with increase in temperature. Linear polarization study showed that this inhibitor affects the anodic site of the corrosion process, while the cathodic site remained unperturbed, thus, expired ofloxacin can be categorized as anodic inhibitor. The adsorption process obeys Langmuir's adsorption isotherm.

### ARTICLE INFO

#### Article History

Received: October, 2021

Received in revised form: October, 2021

Accepted: November, 2021

Published online: December, 2021

### KEYWORDS

Corrosion inhibitor; expired ofloxacin; polarization; temperature; adsorption isotherm.

### INTRODUCTION

Corrosion of metals has continued to be one of the major problems facing industries today, with attendant consequences ranging from environmental contamination by oil or chemical spillage leaked from the corroded pipe line, loss of resources due to spillage and subsequent clean-up, and to the loss of aquatic and human lives. The financial implication of corrosion is estimated to be about 3% to 5% of industrialized countries' gross national product (Uhlig, 1949). The oil and gas industries lose about \$1.372 billion annually (Champion Technology, 2012). Many of the reported oil pipeline failure in oil and gas industries in the Niger Delta area of Nigeria were linked to corrosion (Achebe *et al.*, 2012). Accordingly, corrosion represents a huge industrial setback which must be overcome. However, corrosion is a phenomenon which is almost impossible to completely prevent; nevertheless, it is possible to control it (Brondel *et al.*, 1994). Mild steel is an iron alloy that contains less than 0.25 % carbon. Steel is an excellent choice of structural material due to its high flexural and compressive strength, comparative cheapness and availability. However, one of the major flaws of mild steel is its susceptibility to corrosion. Nevertheless, mild steel is used to handle aggressive solutions in industries (e.g HCl and H<sub>2</sub>SO<sub>4</sub>) during processes (Noor, 2005; Popova *et al.*, 2003),

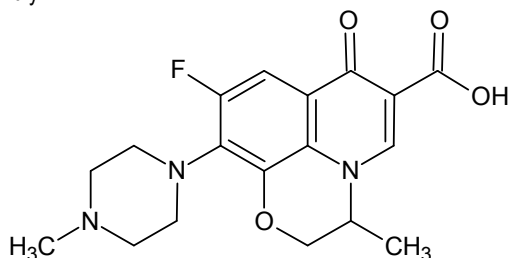
Corrosion is the destructive attack of a material on reaction with its environment, corrosion of metals is an electrochemical process where metals are oxidized to their natural form on exposure to air and water and in the presence of electrolyte. Strong acid like HCl and H<sub>2</sub>SO<sub>4</sub> are highly corrosive and they tend to aggravate the corrosion process. These acids are however used in industries to clean the metal surfaces in processes such as pickling and descaling. To mitigate the corrosion process, inhibitors are added to these solutions to slow down the onset of corrosion. The most effective inhibitors are inorganic salts like chromates. The negative impact of these salts on the environment has outweighed their usefulness as corrosion inhibitors. Therefore, there is a need for environmentally friendly alternative. The focus of the search for new inhibitors is on relatively non-toxic organic compound. The most effective being electron rich compounds possessing O, N, S, and  $\pi$  electrons. These compounds interact with the metal surface by adsorbing onto it, thereby forming a thin film of metal inhibitor complex on the metal surface, hence, a barrier is created between the metal surface and the surrounding corrosive environment.

The use of pharmaceutical products as a safer alternative to conventional inhibitors has been advocated by many researchers (El-Naggar, 2007; Shukla *et al.*, 2009; Singh and

Quraish, 2010). Expired drugs have also been shown to exhibit corrosion inhibition efficiency (Quraishi & Rawat, 2000; Hosseini, *et al.*, 2003; Prabhu, *et al.*, 2007). In line with the above assertion, we seek to investigate the potential of expired ofloxacin (herein referred to as inhibitor) as corrosion inhibitor of mild steel in 1 M HCl solution. As this line of research would provide an alternative way to dispose expired drugs which is cost effective and environmentally friendly.

## MATERIALS AND METHODS

Analar grade reagents were used throughout this work without further purification. Solution preparations were done using distilled. Expired ofloxacin was obtained from NAFDAC office in Kaduna, Nigeria. It was manufactured in China by Jiangsu pengyao pharmaceuticals on April, 2012 and expired on April 2016.



Structure of ofloxacin

Mild steel sample used in this work was obtained from Dana Steel Limited, Katsina, Nigeria. The composition of which is 0.3595, 0.267, 0.713, 0.0486, 0.0543, 0.132, 0.0103, 0.114, 0.0069, 0.0171, 0.265, 0.0249, 0.0202, 0.0087, 0.002, 0.00018, 0.0042, 0.97.9 and 0.0165 % for C, Si, Mn, P, S, Cr, Mo, Ni, Al, Co, Cu, W, Pb, Sn, As, Ca, B, Fe, and Sb respectively.

### Coupons Preparation

Test coupons (samples) were prepared by machining the mild steel rods to cylindrical shapes of dimensions 10 mm by 10 mm length and diameter respectively using lathe machine. The surfaces of the coupons were polished with a polishing machine and abraded with emery paper of different grit sizes (80 - 220). The coupons were then washed thoroughly with distilled water, degreased with acetone, dried and stored in a desiccator to prevent atmospheric exposure.

### Corrosion Testing using Weight Loss Method

The experiment was carried out using a thermostated water bath at 30 and 50 °C. The coupons were weighed and then immersed in 100 cm<sup>3</sup> of 1 M HCl solution with and without addition of different concentrations of the inhibitor (100, 200, 300, 400 and 500

ppm). After 3 hours, the specimens were taken out, washed, dried, and re-weighed. The weight loss was determined using equation (1). The inhibition efficiencies (*IE*%) and the degree of surface coverages ( $\theta$ ) of the inhibitor on the corrosion of mild steel were calculated using equations (2) and (3) respectively.

$$W = W_1 - W_2 \quad (1)$$

Where  $W_1$  and  $W_2$  are the initial and final weights of the coupons respectively

$$IE \% = \frac{W_o - W_i}{W_o} \times 100 \quad (2)$$

$$\theta = \frac{W_o - W_i}{W_o} \quad (3)$$

$W_o$  and  $W_i$  are the weight loss in the absence and presence of inhibitors respectively.

### Electrochemical (Linear Polarization Resistance) Study

Linear polarization measurements were carried out using a cylindrical coupon embedded in resin plastic mount with exposed surface of 4.713 cm<sup>2</sup>. The electrode was polished with different grades of silicon carbide paper (220 - 800), it was then rinsed with distilled water and dried with acetone. The study was conducted at ambient temperature



using potentiostat; NOVA PD STAT 101.1 and electrode cell containing 200 cm<sup>3</sup> of electrolyte maintained in static condition, with and without inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (SEC) as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic measurements were then made from -1.5 to +1.5 V versus OCP at a scan rate of 0.002 V/s, and the corrosion currents were registered. The corrosion current density ( $i_{corr}$ ) and corrosion density ( $E_{corr}$ ) were determined from the Tafel plots of potential  $E$  versus current  $\log i$ . The inhibition efficiency ( $IE\%$ ) was calculated as follows:

$$IE\% = \frac{i_{corr} - i_{corr}^0}{i_{corr}} \quad (4)$$

$i_{corr}$  and  $i_{corr}^0$  are the corrosion current densities with and without the addition of inhibitor respectively.

## RESULTS AND DISCUSSIONS

### Weight Loss Method

#### Effect of Inhibitor concentration on the corrosion rate

Table 1 shows the corrosion penetration rates (CPR), surface coverages ( $\theta$ ) and inhibition efficiencies ( $IE\%$ ) obtained from weight loss measurements for mild steel corrosion in 1 M HCl in the absence and presence of different concentrations of inhibitor at 30 °C after 3 hours immersion time. The results revealed decrease in CPR on increasing inhibitor concentration; which could imply increase difficulty of metal dissolution as a result of interaction with the inhibitor molecules. Both inhibition efficiency and surface coverage increased with increase in inhibitor concentration. This showed that ofloxacin is a fairly good corrosion inhibitor. This is understandable considering the chemical structure of the compound, as it contains various donor atoms like O and N and a number of  $\pi$ -electrons. It is therefore apparent, that this inhibitor would be able to adsorb onto the surface of mild steel via its electron donor atoms, creating a barrier between the mild steel and hydrochloric acid medium these correlates the observation made by other researchers (Singh *et al.*, 2012).

**Table 1:** Corrosion penetration rate, inhibition efficiency and surface coverage for the corrosion of mild steel at various concentrations of expired Ofloxacin at 3 h immersion time

Concentration, ppm	CPR, mm/yr	IE %	$\theta$
0	17.34	0.00	0.0000
100	5.52	68.18	0.6818
200	3.94	77.27	0.7727
300	3.94	77.27	0.7727
400	2.37	86.36	0.8636
500	1.58	90.90	0.9090

#### Effect of Temperature

The effect of temperature on the inhibition efficiency of the studied inhibitor was investigated at 30 and 50 °C. There was a decline in the inhibition efficiency at the temperature of 50 °C (Table 2). This could be attributed to the fact that the protective layer formed by the inhibitor on the surface of mild steel is unstable at elevated temperature,

hence as the temperature was increased, desorption of the inhibitor molecules begins to occur, and this is commonly observed when the interaction between the inhibitor and the mild steel is via electrostatic attraction (physisorption). Similar observation was reported by Fouda *et al.*, 2016 and Owate *et al.*, 2014.

**Table 2:** Corrosion penetration rate, inhibition efficiency and surface coverage for the corrosion of mild steel at various concentrations of expired ofloxacin at 30 and 50 °C after 3 hours immersion time

Concentration, ppm	30 °C			50 °C		
	CPR, mm/yr	IE %	$\theta$	CPR, mm/yr	IE%	$\theta$
0	17.34	0.00	0.0000	29.19	0.00	0.0000

Corresponding author: Auwal, S. H. ✉ [saadahm82@yahoo.com](mailto:saadahm82@yahoo.com) Department of Chemistry, Ahmadu Bello University, Zaria. © 2021. Faculty of Tech. Ed, ATBU Bauchi. All rights reserved

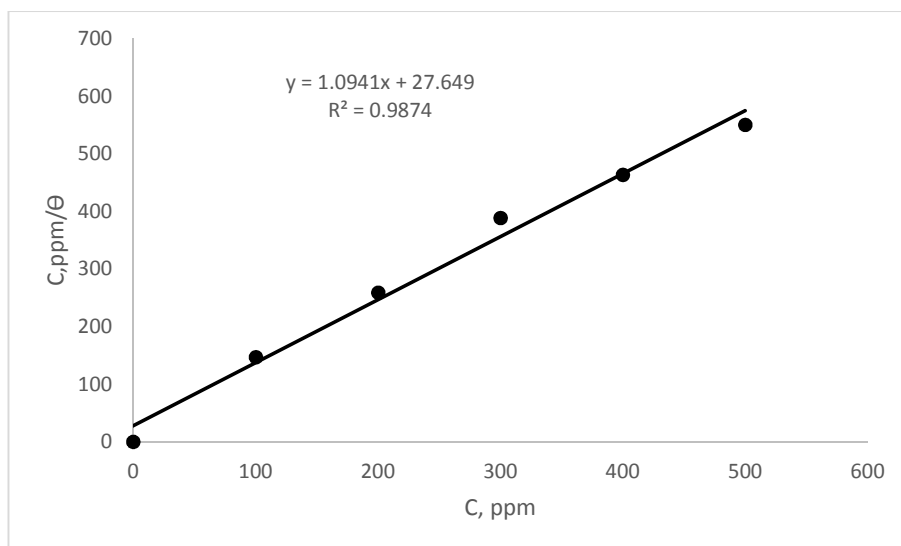
	30 °C			50 °C		
100	5.52	68.18	0.6818	11.83	59.46	0.5946
200	3.94	77.27	0.7727	7.88	72.97	0.7297
300	3.94	77.27	0.7727	6.31	78.38	0.7838
400	2.37	86.36	0.8636	5.52	81.08	0.8108
500	1.58	90.90	0.9090	5.52	81.08	0.8108

### Adsorption Isotherm

The likely mode of adsorption of the inhibitor molecules onto the surface of mild steel was obtained by subjecting the experimental data to Langmuir adsorption isotherm. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species. The equation of the isotherm is given by equation (5):

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

$C$ ,  $\theta$  and  $K_{ads}$  are the concentration, surface coverage and equilibrium constant of adsorption respectively. Plot of  $C/\theta$  against  $C$  gives a straight line, with a slope approximately equals unity (Figure 1). The slight deviation from unity is generally attributed to the interaction of the adsorbed inhibitor molecules on the heterogeneous steel surfaces.



**Figure 1:** Plot of  $C/\theta$  against  $C$  for the corrosion inhibition of mild steel by expired ofloxacin in 1 M HCl solution at 30 °C

### Linear Polarisation Resistance Study

Linear polarization resistance study was made at 500 ppm inhibitor concentration. The result is shown in Table 3. The result showed significant increase in polarization resistance in the presence of inhibitor compared to the blank solution, likewise the corrosion current density of the inhibited system is significantly less than that of the blank. These observations point to fact that there is less ions in the inhibited system, which is due to increased difficulty of metal

dissolution upon addition of inhibitor. The value of cathodic Tafel constant seemed to be unperturbed in the presence of the inhibitor, however, a difference was observed in the values of anodic Tafel constants of the inhibited and uninhibited systems. This indicates that the inhibitor acts as an anodic inhibitor, affecting the anodic site of the corrosion process.

The inhibition efficiency calculated from the polarization resistance compares well with the one obtained from weight loss method.



**Table 3:** Data obtained from polarization resistance study of the corrosion inhibition of mild steel in the presence of 500 ppm expired ofloxacin in 1 M HCl

	Blank	Inhibited solution
Polarisation Resistance	7.998	94.347
Corrosion Potential ( $E_{corr}$ (calc))	-1.0919	-0.8101
Corrosion Potential ( $E_{corr}$ (obs))	-1.0794	-0.84981
Current Density ( $I_{corr}$ )	0.008409	0.000373
Anodic Tafel Constant ( $\beta_a$ )	0.36937	0.18404
Cathodic Tafel Constant ( $\beta_c$ )	0.26666	0.26666
Corrosion rate (mmpy)	97.711	4.3325
Inhibition Efficiency (%)	0.00	95.56

### CONCLUSION

An investigation was carried out on the corrosion inhibition of mild steel using expired ofloxacin in 1 M HCl solution. Data Obtained indicates that expired ofloxacin is a fairly good corrosion inhibitor. Inhibition efficiency increases with increase in inhibitor concentration and decreases with increase in temperature suggesting physical adsorption of the inhibitor onto the surface of mild steel. Linear polarization study also suggests that the inhibitor is anodic type, affecting anodic site of the corrosion process.

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