# Experimental Approach for the Performance of EXPIRED Drug (Isoniazid) as Corrosion Inhibitor in Corrosive Environment

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*Authors' contributions*

This work was carried out in collaboration between all authors. Author OEO designed the study, managed the literature searches, performed the design analysis, wrote the protocol and wrote the first draft of the manuscript. Authors JOB, DTO, GYE and BAA managed the draft and make necessary correction. All authors read and approved the final manuscript

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## ABSTRACT

The development of expired drugs into directly applicable corrosion inhibitors for metals in acidic media, will help not only help to solve the global problem of corrosion but will also offer legal and profitable outlets for extending the cradle to grave life of those materials and eliminate the need for their illegal resale as currently happens in many developing countries such as Nigeria. The expired, biodegradable and environmental drug; Isoniazid was evaluated for corrosion inhibition capability for API5L steel in 0.5M $H_2SO_4$ environment. Electrochemical Impedance Spectroscopy (EIS) reveals a drastic drop in corrosion rate when the pulverized form of expired isoniazid drug was introduced into 0.5M sulphuric acid environment containing immersed steel samples. The impedance diagram shows the same trend (one capacitive loop); however, the diameter of this capacitive loop increases with increasing concentration. The presence of the inhibitor increases the impedance but does not change other aspects of the behaviours. EIS showed that expired isoniazid drugs inhibits corrosion in mild steel in 0.5M $H_2SO_4$ in a mixed manner. Conversely, the

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rate of weight loss in the environment decreased with increasing concentration of expired isoniazid in the environment. Surface Analysis shows a progressive covering and thickening of adsorbed surface layer of expired isoniazid drug film on the immersed API5L steel surface with increasing concentration of the expired drug in the acid environment. The corrosion inhibition was considered to be via a mixed mode adsorption of a layer of expired isoniazid drug molecules across active corrosion sites, gradually cutting off metal-environment contact and thus shutting the relevant corrosion process. The level and effectiveness of achievable corrosion inhibition tend to increase with increased concentration of the expired isoniazid drug in the metal-acid environment. All other evaluation methods support these conclusions.

## 1. INTRODUCTION

API- 5L- X65 steel is a high-strength low-alloy (HSLA) steel that is mostly used as a construction material for pipelines, pumps, off-shore rigs, tanks, agitators [1]. The low cost of API- 5L -X-65 steel relative to the higher performing steels grade is among the reasons, while it is utilized in several applications. In the industrial sector, a major challenge is usually faced by pipeline steels, where they are affected by corrosion consequent to its exposure to corrosive environment, such as HCl [2]. Industrial processes, such as the use of acids for pickling, cleaning, removal of scales as well as oil well acidizing facilitate corrosion and because of the aggressive nature of this acid, inhibitors are utilized in order to minimize the metals dissolution rate [3]. Organic inhibitors have been reported to be relatively eco-friendly, non-toxic, readily available and sustainable. Their ability to resist decomposition with time as compared to most of the green inhibitors is among the reason why they are the most effective and efficient types of inhibitors. These inhibitor molecules have heterocyclic compounds with polar functional groups (e.g., Nitrogen, Sulfur, Oxygen and Phosphorus) and/or conjugated double bonds with different aromatic systems. Metals are usually protected by inhibitors when the inhibitors adsorb themselves to the substrate and then form a passive layer, thus protecting the metal [4]. Inorganic inhibitors have been put to use in many industrial processes for corrosion protection, but due to some reasons, such as cost, toxicity, preference is given to organic inhibitors [5-8]. Also, green inhibitors from plant extract have been reported to display high inhibition efficiency level in addition to their low cost and availability [9]. However, the debate is that the plant kingdom is likely to diminish slowly if plant materials are used as corrosion inhibitors, which is metals will be offered protection at the detriment of the plant kingdom. Furthermore, the problem of using some plant inhibitors is their instability, which they are readily biodegradable [10].

## 2. MATERIALS AND METHODS

### 2.1 Preparation of Steel Samples

The API 5L X65 pipe was sectioned into figures using angular cutter and the figure was further sectioned as seen in Fig. 1 into sixty-five (65) pieces, then grouped into three (3) pieces to make five set. Set one as blank/control, set two as 0.2 g of inhibitor, set three as 0.4 g of inhibitor, set four as 0.6 g of inhibitor, set five as 0.8g of inhibitor. The three pieces in each set were used for the corrosion test varied days (0, 2, 4, 6, 8, 10) for their respective weight loss process.



**Fig. 1. Prepared (2 x 2 x 0.78) cm sample, ready for suspension into 0.5M $H_2SO_4$ with and without inhibitor**

### 2.2 Preparation of Reagents

100 ml of 0.5 M $H_2SO_4$ was measured and put into the each of fifteen beakers of the same height and diameter, thereafter, placed on the same level ground at the same time.

The varied concentration (0 g, 0.2 g, 0.4 g, 0.6 g, 0.8 g) of the inhibitor (expired drug) were put into the beakers (containers) with label of different grams, stirred and allowed settle for 30 minutes to saturate or dissolved in the environment.

## 2.3 Corrosion Rate determination by Weight Loss Method

The setup of the weight loss experiment is as shown in Fig. 3. The sample was tied such that it would not be able to lose/drop from the thread during suspension into the environment. The sample were suspended completely into the environment. The environment contains 100 ml of 0.5M $H_2SO_4$, with and without inhibitor. The inhibitor in each environment varied in concentration of (0, 2, 4, 6 and 8) grams. Initial weights were recorded on the first day, and other weights were taken on the Second (2), fourth (4), Sixth (6), Eight (8) and Tenth (10) days with the help of weighing balance.

$$CR = \frac{W_i - W_f}{A * \frac{T}{365}}$$

where CR is the corrosion rate in $mg/mm^2$ /yr, W is weight loss in milligrams, A is the total surface area of exposure in $mm^2$, T is the exposure time in days.

The inhibitor efficiency was measured by equation

%I.E = ((CRinh – CR$_{blank}$)/ (CR$_{blank}$)) * 100

where I. E is inhibitor efficiency (percentage), CRinh is corrosion rate of metal with inhibitor and CRblank is corrosion rate of metal without inhibitor.

## 2.4 Surface Analysis

The surface morphology of the API steels consequent to the reaction of the environment with the steel's surface were analyzed with optical microscopy. The API-5L-X65 steel immersed in 0.5M $H_2SO_4$ for 1,200 seconds from the electrochemical test at normal condition was used for the study. Sample in the absence of inhibitor (considered as control) and those exposed at optimum volumes of the inhibitors were subjected to optical microscopic analysis.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Chemical Composition

The elemental composition of the API-5L-X65 steel used for this research is displayed in Table 1.

The elemental composition of the studied API5L steel metal correlates with API standard [11].

The elemental composition of the API5L steel metal was studied and it was observed that the sum of the alloy elements are less than 2% hence, the plain carbon steel is prone to corrosion in a corrosive environment. The percentage carbon composition is 0.12%, which belongs to the class of low carbon steel and that makes it to be ductile and malleable [12-13].

## 3.2 Scanning Electron Microscopy (SEM) Evaluation

Fig. 2(a-c) displays the micrograph of the API5L-X65 steel before immersion and after immersion the in 0.5M $H_2SO_4$ environment with and without inhibitor (isoniazid). Fig. 1a is displaying the morphology of the API5L-X65 steel sample, which has not been immersed into the corrosive environment. Hence, it is as received without any formation of corrosion product on the surface. It is observed from the micrograph in Fig. 2(b and c) that there was a formation of a non-tenacious corrosion product on the control sample surface after immersion in 0.5M $H_2SO_4$ environment with inhibitor (isoniazid). The non-tenacious corrosion product formed as a result of reaction of the steel with the aggressive environment. Thus, increasing the rate at which the steel corrodes. Fig. 2c represents the micrograph of the API steel immersed in the 0.5M $H_2SO_4$ environment, containing 0.8 g of inhibitor. It was observed that the inhibitor adsorbed and was uniformly dispersed on the steel surface, thereby acting as a protective barrier between the steel surface and the corrosive environment. This led to a reduction in the corrosion rate of the steel.

## 3.3 Corrosion Rate against Exposure Time for the API- 5L- X65 Steel Immersed in 0.5M of $H_2SO_4$ without and with (isoniazid) Inhibitor

Fig. 3 displays the plot of corrosion rates against exposure time for the API-5l-X65 steel in 0.5M of $H_2SO_4$ with and without inhibitor. The plots were obtained from the weight loss results. The plot of corrosion rate with time for the API 5L X65 steel immersed in 0.5M of $H_2SO_4$ without and with inhibitor for 10 days is displayed in Fig. 3. It was observed that the corrosion rate increased with increase in the inhibitor's concentration from 0.0g/l to 0.8g/l. Steel sample in inhibitor concentration of 0.8 g/l had the least corrosion rate of 6.42635 mg/mm2 /yr as against the corrosion rate of 50.04989 mg/mm2 /yr for the control (blank) sample. Also, the reduction in corrosion rate, as observed in the increase in the

concentration, amount from 0.0g/l to 0.8g/l, may likely be as a consequence of the electron-rich N atoms of –NH2 group present in isoniazid. In the aqueous acidic solutions, isoniazid may occur either as neutral molecules or in the form of protonated molecules (cations). Generally, the surface of steel becomes positively charged in acid solution and as a result hinders the protonated inhibitors from being attracted towards the mild steel surface of positive charge due to the electrostatic repulsion. However, ions like sulfur which are known to bear smaller

degree of hydration could bring in excess negative charges around the interface, thus allowing more of the positively charged inhibitor molecule to be adsorbed. Also, the adsorption of the protonated inhibitor is by electrostatic interactions that occur between the positively charged molecules and the negatively charged metal surface. Thus, resulting in a decrease in corrosion rate, as reported by Odozi et al. [14] Abdallah et al. [15], Mehdi et al. [16,12] and Mohammad et al. [17]

**Table 1. Elemental composition of the API-5L-X65 steel**

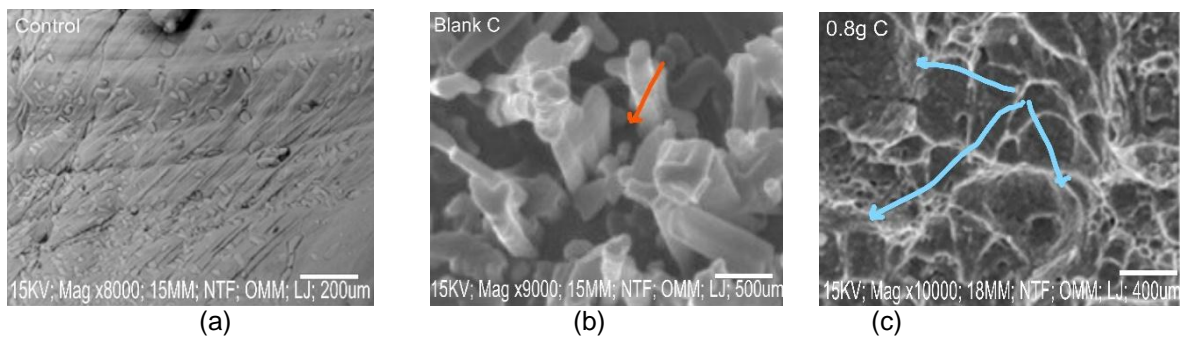| Element | C | Mn | Si | Cu | P | S | Cr | Ni | Fe |
|---------|------|------|------|-------|------|-------|-------|-------|------|
| Metal (wt %) | 0.13 | 1.35 | 0.25 | 0.012 | 0.02 | 0.002 | 0.024 | 0.014 | Bal. |



(a)  (b)  (c)

**Fig. 2. Scanning electron micrographs of API5L Steel samples (a) before immersion, (b) after immersion without inhibitor, (c) after immersion with inhibitor, in 0.5M H$_2$SO$_4$ environment**
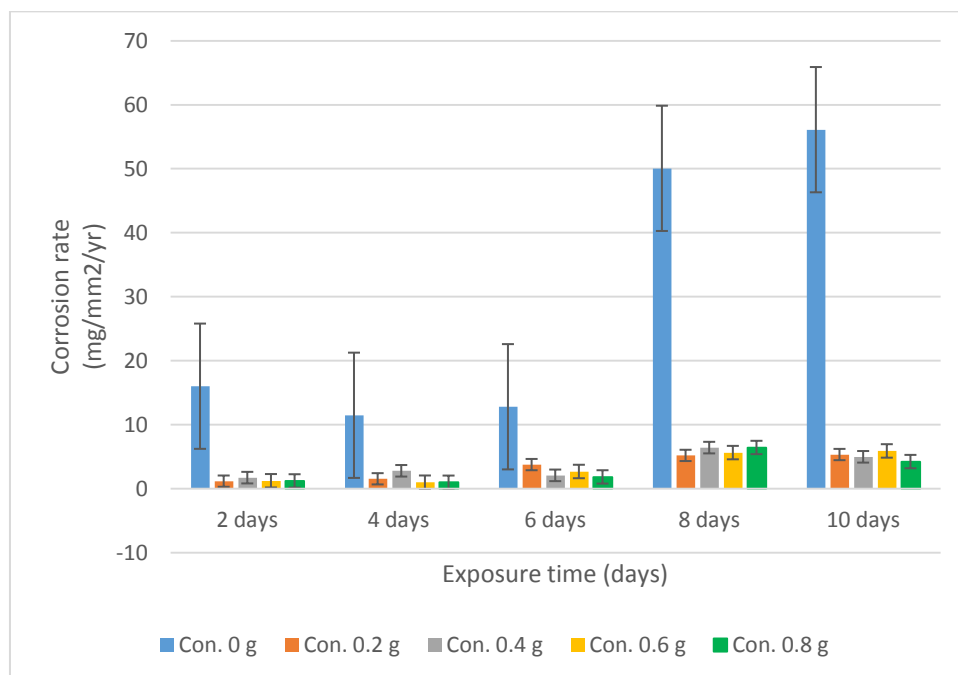


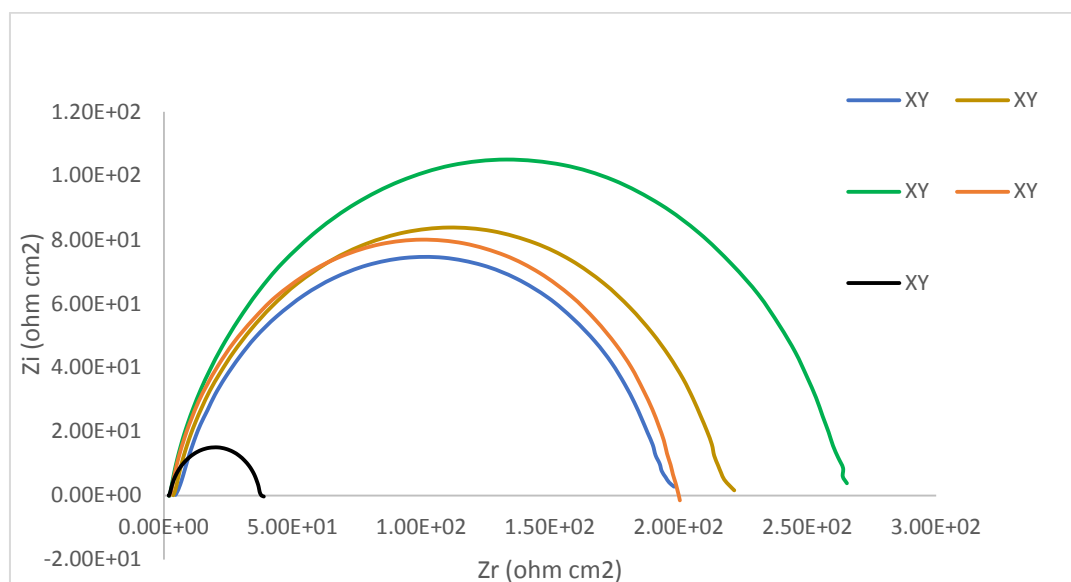**Fig. 3. Weight loss for the API5L steel at varied days in 0.5M of H$_2$SO$_4$ environment**

**Fig. 4. Nyquist plots for the API5L steel in 0.5M $H_2SO_4$ solution in the absence and presence of different concentrations of inhibitor**

### 3.4 Electrochemical Impedance Spectroscopy (EIS)

The corrosion behavior of API5L steel in 0.5M $H_2SO_4$ solution in the absence and presence of the studied inhibitor was investigated by EIS method. Fig. 4 shows the Nyquist plots for API5L steel in 0.5M $H_2SO_4$ solution in the absence and presence of different concentrations of inhibitor. The Nyquist plots were regarded as one part of a semicircle. The impedance diagram shows the same trend (one capacitive loop); however, the diameter of this capacitive loop increases with increasing concentration. The presence of the inhibitor increases the impedance but does not change other aspects of the behavior. These results support the results of polarization measurements that the inhibitor does not alter the electrochemical reactions responsible for corrosion. It inhibits corrosion primarily through its adsorption on the metal surface [18].

## 4. CONCLUSIONS

The results obtained from this study suggest that isoniazid is a good inhibitor for combating industrial corrosion of API 5L X65 steel in 0.5M $H_2SO_4$ environment. Also, the inhibitor high surface coverage and good inhibition efficiency.

## DISCLAIMER

The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.

## COMPETING INTERESTS

Authors have declared that no competing interests exist.

## REFERENCE

1. Sherif ESM, Almajid AA, Khalil AK, Junaedi H, Latief FH. Electrochemical Studies on the Corrosion Behavior of API X-65 Pipeline Steel in Chloride Solutions, Int. J. Electrochem. Sci. 2013;8:9360–9370.
2. Junaedi S, Al-Amiery AA, Kadihum A, Kadhum AAH, Mohamad AB. Inhibition Effects of A Synthesized Novel 4-Aminoantipyrine Derivative on the Corrosion of Mild Steel In Hydrochloric Acid Solution Together With Quantum Chemical Studies, Int. J. Mol. Sci. 2013;14:11915–11928.
3. Firdhouse MJ, Nalini D. Corrosion Inhibition of Mild Steel in Acidic Media by 5'-Phenyl-2', 4'-Dihydrospiro [Indole-3, 3'-

Pyrazol]-2(1H)-One, J. Chem. 2013;9:835–365.

4. Bothi RP, Sethuraman MG. Natural Products as Corrosion Inhibitors for Metals in Corrosive Media: A Review, Mater. Lett. 2008;62:113–116.

5. Abdel-Gaber AM, Abd-El-Nabey BA, Saadawy M. The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract', Corrosion Science. 2009;51(5):1038–1042.
DOI: 10.1016/j.corsci.2009.03.003.

6. Asipita SA, Mohammad I, Muhd Zaimi A, Zaiton A, CheSobry A, Jahangir M. Green BambusaArundinacea Leaves Extract as a Sustainable Corrosion Inhibitor In Steel Reinforced Concrete, J. Clean. Prod. 2014;67:139–146.

7. Abdulrahman AS, Mohammad I, Mohammad SH. Corrosion inhibitors for steel reinforcement in concrete: A review', Scientific Research and Essays. 2011;6(20):4152–4162.
DOI: 10.5897/sre11.1051.

8. Obolo OE. Electrochemical Gravimetric and Quantum Chemical investigation of expired drugs as corrosion inhibitor for API5L steel in 0.5m $H_2SO_4$, M. Eng Final Seminar, FUTA, Akure, Nigeria; 2021.

9. Patel NS, Jauhari S, Mehta GN, Al-Deyab SS, Warad I, Hammouti B. Mild Steel Corrosion Inhibition by various Plant Extracts in 0.5 M H2SO4. Int. J. Electrochem. Sci. 2013;8:2635–2655.

10. Rajendran S, Sri V, Arockiaselvi J, Amalraj AJ. Corrosion Inhibition by Plant Extracts – An overview. Bullet. Electrochem. Sci. 2005;8:367–377.

11. American petroleum institute "API 5L; 2012.

12. Shittu S. et al. Comparative Study of the Effect of Imidazole and Tryethylene-Tetra-Amine on the Corrosion Behaviour API-5L-X65 Steel in 1M HCl Environment', International Journal of Mechanical and Production Engineering Research and Development. 2020;10(2): 443–452.

13. Yarong Song, Guangming Jiang, Ying Chen, Peng Zhao, Yimei Tian. Effects of chloride ions on corrosion of ductile iron and carbon steel in soil environments. Nature Publishing Group. 2017;7:1-13.

14. Odozi NW, Babalola JO, Ituen EB, Eseola AO. Imidazole Derivatives as Nobel Effective Inhibitor of Mild Steel Corrosion in Aqueous Sulfuric Acid, Am. J. Phy. Chem. 2015;4(1):1–9.

15. Abdallah M, Zaafarany I, Khairou K, Sobhi M. Inhibition of Carbon Steel Corrosion by (Iron III) and Imidazole in Sulfuric Acid, Int. J. Electrochem. Sci. 2012;7:1564–1579.

16. Mehdi S, Maryam D, Shirin E. Theoretical Studies on the Corrosion Inhibition Performance of Three Amine Derivatives on Carbon Steel, J. Taiwan Institute of Chem. Eng., Elsevier J. 2016;62:313–321.

17. Mohammad HG, Maryam DA DFT and Molecular Dynamics Study on Inhibitory Action of Three Amine Derivatives on Corrosion of Carbon Steel, J. Appl. Chem. Res. 2017;11(1):7–20.

18. Al-Shafey HI, Abdel Hameed RS, Ali FA, Aboul-Magd AS, Salah M. Effect of Expired Drugs as Corrosion Inhibitors for Carbon Steel in 1M HCL Solution. Int. J. Pharm. Sci. Rev. Res. 2014;27(26):146-152.