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Inhibition of aluminum corrosion in hydrochloric acid solution using different inhibitors

A graduation research project

Submitted to the Department of Chemistry in partial fulfillment of the requirements for the completion of the degree of Bachelor of Science in Chemistry

By

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ABSTRACT

Inhibition of Aluminum corrosion in 1M hydrochloric acid solution using different inhibitors has been studied by weight loss and hydrogen evolution measurement. It was found that the (E)-2((2-phenylhdrazono) methyl) phenol, O-phenylenediamine and Hydrazine Hydrate 80 % act as a good inhibitors for aluminum corrosion in the acid solution and the best one was (E)-2((2-phenylhdrazono) methyl) phenol. On the other side the 2,4-Dinitrophenylhydrazine accelerate the Al corrosion. The inhibitory action of the used inhibitors was discussed in view of the adsorption of its components on aluminum surfaces. It was found that the adsorption of these compounds on the Al surface follows the Freundlich adsorption isotherm. Also, the inhibition efficiency (IE) increases as the inhibitor concentration is increased. The SEM images confirm the formation of protective layer on the metal surface. The inhibition efficiencies obtained from gasometry and weight loss measurements are in good agreement with each other

ملخص

تم دراسة تثبيط تآكل الألومنيوم في M1 من حمض الهيدروكلوريك باستخدام مثبطات مختلفة و بطرق حكم مختلفة و هي طريقة فقدان الوزن وطريقة قياس تصاعد الهيدروجين. وقد تبين أن:

(E)-2((2-phenylhdrazono) methyl) phenol, O-phenylenediamine and Hydrazine Hydrate 80 %

بمثابة مثبطات جيدة لتآكل الألومنيوم في محلول حمض الهيدروكلوريك وأفضلهم كان:

(E)-2((2-phenylhdrazono) methyl) phenol

على الجانب الآخر وجد أن:

2,4-Dinitrophenylhydrazine

مسرع للتآكل. ونوقش ميكانيكية التثبيط للمثبطات المستخدمة من وجهة نظر إدمصاص المثبط على أسطح الألومنيوم. وقد وجد أن ادمصاص هذه المركبات على سطح الألومنيوم يتبع امتزاز الأيزوسيرم Freundlich. أيضا وجد أن كفاءة التثبيط (IE) يزيد بزيادة تركيز المثبط. كذلك صور SEM تؤكد على تشكيل طبقة واقية على سطح المعدن. ووجد أن كفاءات التثبيط التي تم الحصول عليها من قياسات تصاعد الغاز وفقدان الوزن هي في اتفاق جيد مع بعضها البعض.

CHAPTER 1 INTRODUCTION

Aluminium, is a metallic material that has properties that allow quite different uses and somewhat opposites. Due to its resistance to corrosion in many media and their mechanical properties, reflected in a low density and good mechanical tensile strength, it is a material with excellent characteristics for use in construction and aerospace industry [1]. One of the most important applications of Al and its alloys is found in aluminium-air technology, which was of particular interest for its application to electric vehicle propulsion as well as its low production cost and the existence of a large base for manufacture and distribution [2]. Acid solutions have significant application in industrial processes which includes acid cleaning, descaling and pickling of metallic structures, oil well acidification, electroplating and electro polishing which are usually accompanied by considerable dissolutions of the metal. A useful method of protecting metals like Al and alloys deployed in service in aggressive environments against corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and hence reduce the corrosion rate [3, 4]. Adsorption depends mainly on the charge and the nature of the metal surface, electronic characteristics of the metal surface, adsorption of solvent and other ionic species, temperature of corrosion reaction and on the electrochemical potential at solution interface and the type of electrolyte [5,6]. Originally, inorganic inhibitors such as zinc chromate, polyphosphate and nitrite were used as inhibitors. The efficacy of inhibitor to act as a successful corrosion inhibitor is its ability to get adsorbed on the surface of the metal [7]. Therefore, the corrosion rate in the presence of the inhibitor may be taken to represent the number of potentially corroding sites that remain after blockage via the inhibitor adsorption. It has been observed [8] that the extent and mode of adsorption of corrosion inhibitors on the metal surface depend mainly on certain physical-chemical properties of the molecule such as functional groups, aromaticity, steric factors, electron density at the donor atoms and π orbital character of the donating electrons, and also on the electronic structure of the molecules.

Recent awareness emphasizes that plant products containing compounds like amines, tannins, alkaloids, saponins, essential oils, flavonoids, organic and amino acids are known to exhibit corrosion inhibiting action for steel and aluminium in acidic environment [9-15]. Such organic compounds are known to contain oxygen, nitrogen, phosphorus, and sulphur, in a conjugated system [8] and they inhibit via adsorption of the molecule on the metal surface thereby blocking the active corrosion sites [16].

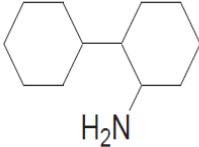
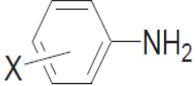
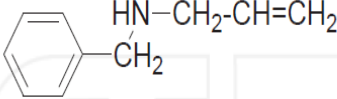
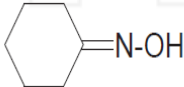
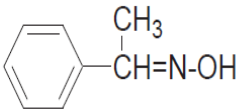
A proposed research project aims to study the inhibition of aluminum corrosion in 1M hydrochloric acid using different inhibitors. we will study the corrosion using weight loss method and the method of measuring hydrogen evolution method. Also will be use different modern instruments such as X-ray diffraction measurement and microscopic examination using scanning electron microscope.

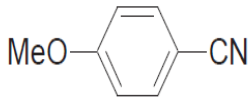
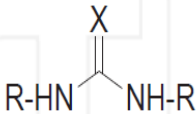
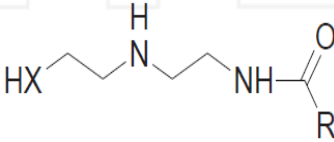
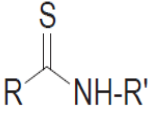
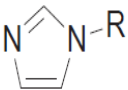

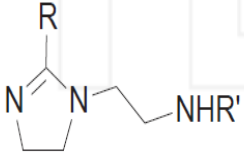
CHAPTER 2 LITERATURE REVIEW

In most industries whose facilities are constituted by metallic structures, the phenomenon of corrosion is invariably present. This problem originates very important material and economic losses due to partial or total replacement of equipment and structures, and plant-repairing shutdowns. Material losses and corrosion consequences are priced so high that in some countries like the U.S. and England these factors have been estimated from 3 to 4% of the GDP. Corrosion not only has economic implications, but also social and these engage the safety and health of people either working in industries or living in nearby towns. The oil industry in Mexico is one of the most affected by corrosion because this phenomenon exerts its effects from the very moment of oil extraction on, causing a constant struggle against it. The use of corrosion inhibitors (CIs) constitutes one of the most economical ways to mitigate the corrosion rate, protect metal surfaces against corrosion and preserve industrial facilities [17,18]. Inorganic CIs are those in which the active substance is an inorganic compound. This is one of the simplest ways to improve the passivity of a metal by adding electropositive metal salts to the medium. These metal ions must have a more positive redox potential more positive than the metal constituting the surface to be protected and also a more positive potential than that required for discharging a proton so that the electropositive metal to be reduced is deposited on the surface. The deposited metal promotes the cathodic depolarization by overvoltage reduction and formation of an adherent deposit. Among the metals used for this purpose are: mercury (Hg), palladium (Pd), iridium (Ir), platinum (Pt), rhodium (Rh) and rhenium (Re).

Moreover, there are inorganic anions providing passivation protection to metal surfaces through their incorporation into the oxide layer; the most widely used of these are: chromate (CrO_4^{2-}), nitrate (NO_2^-), molybdate (MoO_4^{2-}), phosphate (H_2PO_4^-) and silicates [19].

Organic inhibitors have been the most widely used in petroleum refining processes because of their ability to form a protective layer on the metal surface in media with high hydrocarbons content. At present there are a number of organic inhibitors belonging to different chemical families i.e. fatty amides [20,21], pyridines [22-24], imidazolines [25-28] and other 1,3-azoles [29-31] and polymers [32] have showed excellent performance as CIs (Table 1) [33].

Chemical family	Structure	Main application
	Alkylamines (n = 2-12) $\text{CH}_3-(\text{CH}_2)_n-\text{NH}_2$ Diamines (n = 2-8) $\text{H}_2\text{N}-(\text{CH}_2)_n-\text{NH}_2$	
Primary amines and diamines	Cycloalkylic 	CIs for acid media
	Aromatic (X = H, NO ₂ , CH ₃ , Cl, COOH) 	
Secondary amines	Benzilamines 	CIs for carbon steel in acid media
	Etoxilated amines $\text{CH}_3-(\text{CH}_2)_n-\text{NH}-(\text{OCH}_2\text{CH}_2)_n$	
Oximes	Alkylloximes 	CIs for carbon steel in acid media
	Aromatics 	

Chemical family	Structure	Main application
Nitriles	Alkyl nitriles $C_{17}H_{35}-CN$ Aromatics 	CIs for carbon steel in acid media
Ureas y thioureas	 $X = O, S, R = \text{alkyl, aryl}$	CIs for copper alloys and carbon steel in acid media
Amides y thioamides	Amides  Thioamides  $R, R' = \text{alkyl}$	CIs for carbon steel in acid media
Imidazoles	 $R = \text{alkyl, aryl}$	CIs for copper alloys and carbon steel in basic media
Benzoazoles	 $X = N-R, S, O$	CIs for copper alloys and carbon steel in basic media
Imidazolines	 $R = \text{alkyl, aryl}; X = NH_2, NHR, OH$	CIs for carbon steel in acid media


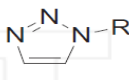
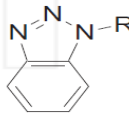
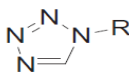
Chemical family	Structure	Main application
Pyridines	 $X = \text{CH}_3, \text{Br}, \text{OR}$	CIs for carbon steel in acid media
Triazoles	 $R = \text{alkyl, aryl}$	CIs for copper alloys in basic media
Benzotriazoles	 $R = \text{alkyl, aryl}$	CIs for copper alloys in basic media
Tetrazoles	 $R = \text{alkyl, aryl}$	CIs for copper alloys in basic media
Polyvinyls	$\text{R}-(\underset{\text{R}'}{\text{C}}\text{H}=\text{C}\text{H})_n$ $\text{R, R}' = \text{alkyl, aryl, heterocyclics}$	CIs for carbon steel in acid media
Polyesters	$\text{R}-(\text{OCH}_2\text{CH}_2)_n$ $\text{R} = \text{alkyl, aryl}$	CIs for carbon steel in acid media

Table 1: Organic corrosion inhibitors widely used in petroleum refining processes

The aim of adding inhibitors in low concentrations to corrosive media is to delay the reaction between the metal and the corrosive species in the medium. CIs act by adsorbing either ions or molecules onto the metal surface, generally reducing the corrosion rate by blocking the anodic and/or cathodic reactions. In spite of much inorganic, organic and polymeric compounds have been showed good performances as CIs for different metals and alloys, many of these compounds are toxic and do not fulfill completely the requirements imposed by the environmental protection standards.

2.1 Generalities about corrosion [17]

The term corrosion can be defined as the interaction (electrochemical reaction) of a metal with the surrounding environment, causing a slow, steady, and irreversible deterioration in the metal, in both physical and chemical properties. The corrosion causes very important material and economical losses due to partial or total replacement of equipment and structures, and plant-repairing shutdowns. Corrosion not only has economic implications, but also social and these engage the safety and health of people either working in industries or living in nearby towns. The petroleum industry is one of the most affected by corrosion due to the presence of many corrosive substances in the crude oil, which affect equipments and pipelines from the extraction of crude oil to the transportation of final products.

The factors that can cause corrosion can be identified as:

- Physical
- Chemical
- Electrochemical
- Microbiological

Physical corrosion is caused by impact, stress or exhaustion of the material. Chemical corrosion is caused by oxygen, sulfur, fluorine, chlorine or other gases,

which act directly on the metal under environmental conditions that facilitate this phenomenon. Electrochemical corrosion is a spontaneous process that denotes the existence of anodic and cathodic zones, and an electrolyte; electrical contact between the anodic and cathodic zones is also required (Figure 1).

Microbiological corrosion is the deterioration of a metal that occurs directly or indirectly as a result of the activity of microorganisms such as bacteria and algae. These microorganisms are deposited on the metal, creating a “live” area, using nitrogen, oxygen, hydrogen, and/or carbon from the environment for their metabolic activities, producing metabolites, which can be deposited on the metal promoting corrosion. Biological activity may cause corrosion in a variety of media such as natural water, sea water, petroleum products and oil emulsions.

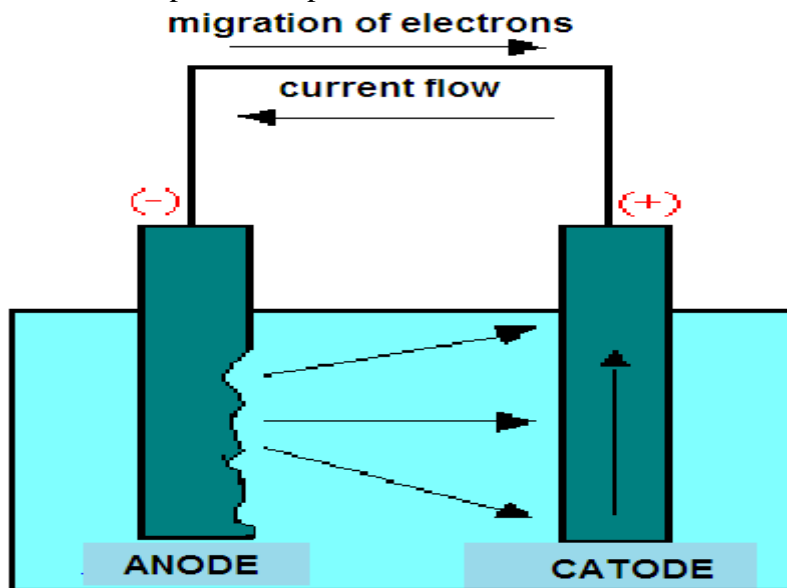


Figure 1. Representation of electrochemical corrosion

According to the environment to which materials are exposed, there are various forms of corrosion: uniform or general, pitting, erosion, stress, cavitation, galvanic and hydrogen embrittlement-blistering. Knowing how corrosion works helps to understand the phenomenon and provide possible solutions to counter the corrosive process.

a. Uniform or general corrosion is the most common, which is characterized by the fact that corrosion occurs uniformly over the metal surface and has a high corrosion rate; the loss of the metal surface occurs through an anodic site, and the appearance of the corroded surface is relatively uniform, but manifests roughness (Figure 2) [34].

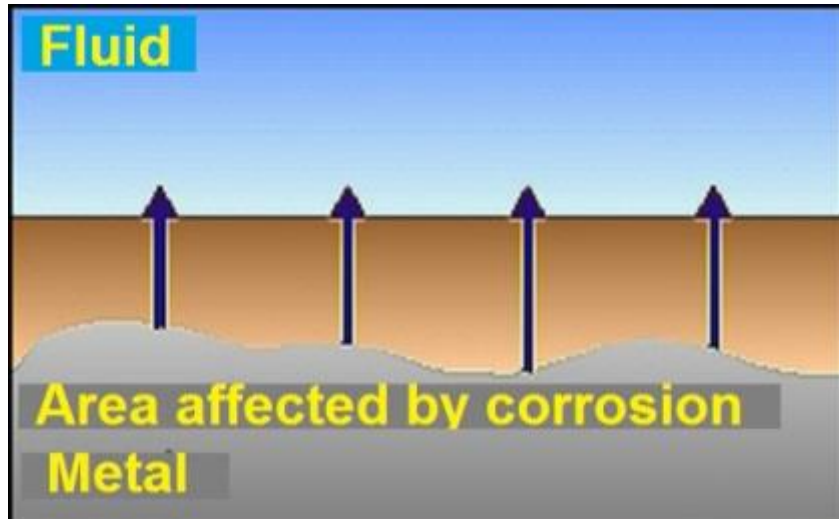


Figure 2. Uniform Corrosion

b. Pitting corrosion: Is a localized attack, where some parts of the metal surface are free of corrosion, but small localized areas are corrode quickly; this occurs when any solid corrosion product or neutralization salts are located on the metal surface, causing deep holes, which is known as pitting (Figure 3); these areas are the most susceptible to the corrosion process [35].

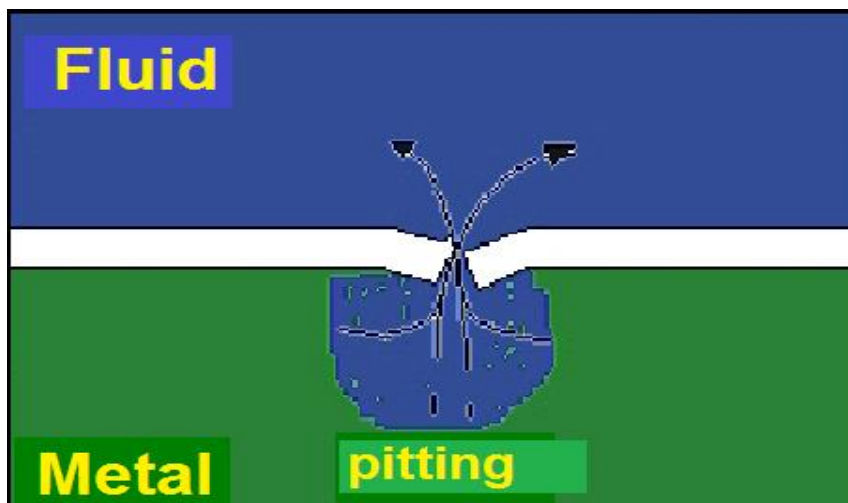


Figure 3. Pitting corrosion

c. Corrosion by erosion: This type of corrosion provokes uniform thinning of the metal surface, which is associated with the exposure to a high velocity fluid, which causes the corrosion product to be stripped from the metal surface, resulting in the exposure of the bare metal, which can be corroded again, causing an accelerated attack, (Figure 4). This type of corrosion is further exacerbated when fluids contain solid particles that are harder than the metal surface, which hit constantly the metal [36].

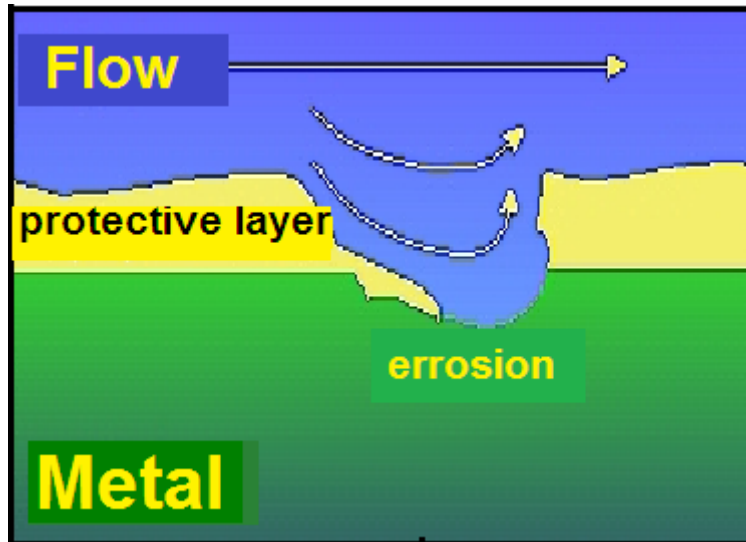


Figure 4. Corrosion by erosion

d. Stress corrosion cracking: This type of corrosion promotes the formation of a fracture in the metal structure due to mechanical stress and a chemically aggressive medium (Figure 5) [37].

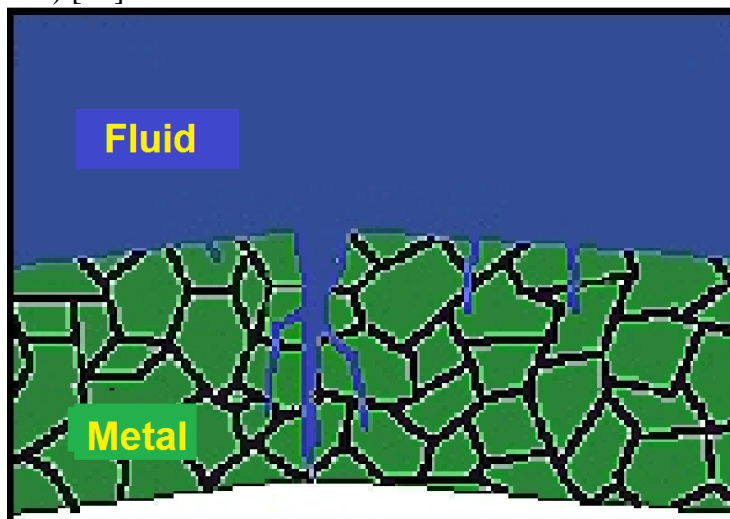


Figure 5. Stress corrosion cracking

e. Galvanic or bimetallic corrosion occurs when there is a potential difference between dissimilar metals immersed in a corrosive solution; the potential difference produces a flow of electrons between the metals, where the less resistant metal is the anode (metal active), and the most resistant is the cathode (noble metal). This attack can be extremely destructive, dramatically accelerating the corrosion rate of the most reactive metal, but the severity degree of galvanic corrosion depends not only on the potential difference between the two metals, but also on the involved surface area ratios, (Figure 6) [38].

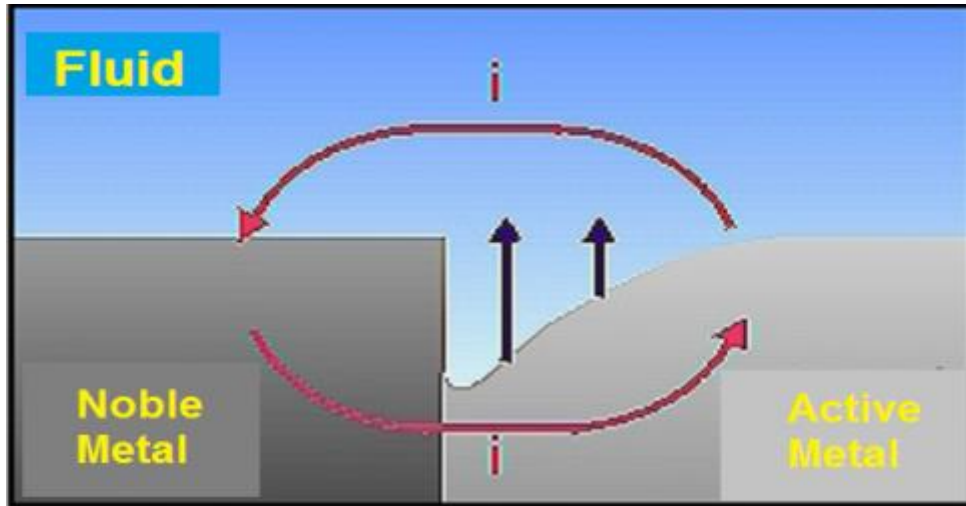


Figure 6. Galvanic corrosion

f. Corrosion by cavitation is a form of erosion caused by the formation and rupture of vapor bubbles in the fluid near the metal surface, causing a sequence of pits in the form of small, but deep cracks (Figure 7) [39].

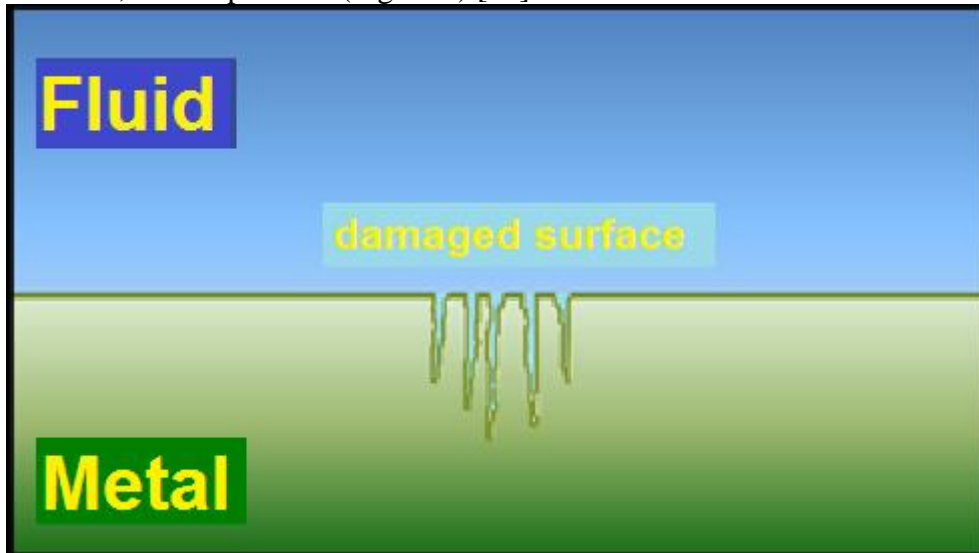


Figure 7. Corrosion by cavitation

g. Corrosion via hydrogen embrittlement and blistering is associated with the hydrogen atoms that are produced on the metal surface in an aqueous medium; a reduction reaction when atomic hydrogen penetrates the metal takes place; the presence of defects allow the interaction between the hydrogen atoms and the metal, forming molecular hydrogen, which being trapped by the metal, provides enough pressure to form blisters, resulting in microcracks, (Figure 8). This type of failure occurs mainly in basic media, where there are compounds such as sulfides and/or cyanides; this corrosion process is also present in plants with catalytic refining processes.

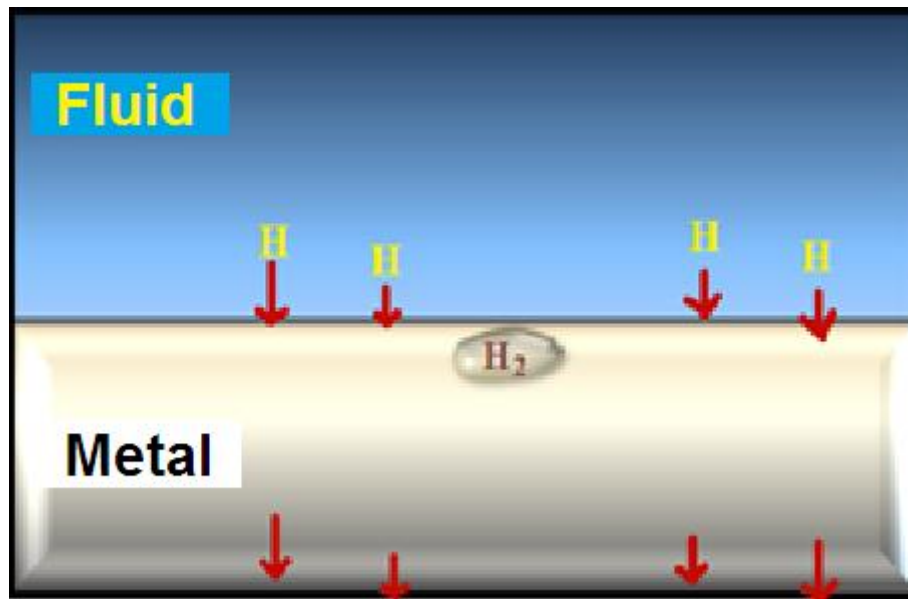


Figure 8. Corrosion by hydrogen embrittlement and blistering.

In this kind of corrosion processes, some hydrogen atoms diffuse through steel and become retained, where they recombine with each other, forming a very strong internal pressure that exceeds the strength of steel, forming blisters.

In most oil refining plants, the reactive metal is iron, which is the major component of the steel present in pipelines and equipment; the electrolyte is water and the corrosive or oxidizing agent is formed by acids, salts, bases, oxygen, etc. One of the most common methods used to reduce corrosion in petroleum refining processes is the application of corrosion inhibitors, which are specific to each process phase, medium and corrosion type [40].

2.2 Corrosion control [41]

In order to control some of the corrosion problems, several preventive measures are taken:

- a. Cathodic protection. This is an effective method to control corrosion on structures either buried or immersed in an electrolyte; according to the operation mode, anodes are classified as impressed current and sacrificial.
- b. Protection with anticorrosive coating. This is mainly used to form a physical barrier between the corrosive environments to protect the structure. It is used mainly with metallic elements exposed to the atmosphere.
- c. Corrosion Inhibitors. These are substances that added in small concentrations (parts per million, ppm) to a corrosive environment decrease the corrosion rate effectively. This method has its main application in the interiors of pipelines, vessels and equipments.

A corrosion inhibition program should be monitored continuously to ensure that it is achieving the desired protection. The corrosion measurement is the quantitative method by which we know the effectiveness of the control that is being carried out, and provides feedback that makes possible to optimize the control and corrosion prevention methods. Particularly in the Petroleum Industry, the monitoring can be done by using the following methods:

- Monitoring feedstocks by chemical analysis to find some of their features and corrosive contents.

- Monitoring corrosives by analysis of bitter waters of batteries (pH, chlorides, sulfides, ammonium thiocyanate and cyanide).
- Corrosion Monitoring: Be made in the following ways:
 - a. Using gravimetric coupons located at places where corrosion is to be measured (Figure 9).



Figure 9. Coupons to measure corrosion

- b. With corrosimetric specimens. These probes are installed at the places to be monitored. A corrosimeter connected to a probe detects a current amount and depending on it, it is known if there is corrosion and the communication speed.
- c. Analyzing the iron and copper contents in the bitter waters of accumulators.
- d. By placing hydrogen probes at the absorber tower.

2.3 Corrosion Inhibitors (CIs)

CIs are either organic or inorganic chemicals, or more commonly, formulations thereof that are added in small amounts (parts per million, ppm) to a corrosive environment in order to delay or decrease the corrosion process of the surface to be protected. Due to the fact that equipment constructed with materials resistant to corrosion is very expensive, it is common to use corrosion inhibitors as a practical, economical and simple alternative.

A recent study in the United States indicated that their industries spent about \$276 billion/year (on what?) and around 900 million/year on about 200 million tons of CIs. This market is shared by about 40% of inorganic inhibitors such as sulfonates and phosphonates (for cooling towers) and 60% of organic inhibitors, for example amines, cyclic amines, quaternary amidoamines, diethylamines, imidazolines and fatty acids, which are primarily used as CIs in the Petroleum Industry, in the production of gas, refineries, oil pipelines and products [42].

The CI formulations generally are made up of one or more active ingredients and suitable vehicles (other additives and solvents) that encourage compatibility with the environment and make viable the active transport to the area to be protected (metal surface).

The properties that must be met by a CI are [43,44]:

- a. Capability of reducing corrosion rates.
- b. The active principle of the CI must be in contact with the metal to be protected.
- c. Must not have side effects.

Sometimes, two components or active ingredients in a formulation may have a higher efficiency when they are mixed than that obtained from the sum of the efficiencies that are obtained when they are used individually at the same concentration. This

effect is known as synergy or synergistic effect and is widely used in the formulation of CIs.

The CI can be classified in different ways [45 ,46].

According to the specific application within the oil refining processes:

- a. Embedding inhibitors.
- b. Blistering inhibitors.
- c. High temperature inhibitors.
- d. Inhibitors for acidic media.
- e. Inhibitors for basic media.
- f. Inhibitors for cooling water.

The CI can also be classified according to the type of material to be protected. In the oil refining processes, CIs are of special interest for carbon steel, in which the major component is iron; and inhibitors for copper-zinc alloys (Admiralty), which are the most common materials used in the design of refineries. CIs can be classified as anodic, which are those that inhibit oxidation of the metal; cathodic, which inhibit the reduction of oxygen; and mixed inhibitors, which inhibit both processes. CIs can also be classified according to the type of compound that forms the active ingredient in the formulation as inorganic, organic and biocides.

2.4 Inhibitor mechanism

The action mechanisms of CIs [47]:

- By adsorption, forming a film that is adsorbed onto the metal surface.
- By inducing the formation of corrosion products such as iron sulfide, which is a passivating species.
- By changing media characteristics, producing precipitates that can be protective and eliminating or inactivating an aggressive constituent.

It is well known that organic molecules inhibit corrosion by adsorption, forming a barrier between the metal and the environment [48]. Thus, the polar group of the molecule is directly attached to metal and the nonpolar end is oriented in a vertical direction to the metal surface, which repels corrosive species, thus establishing a barrier against chemical and electrochemical attack by fluids on the metallic surface (Figure 10).

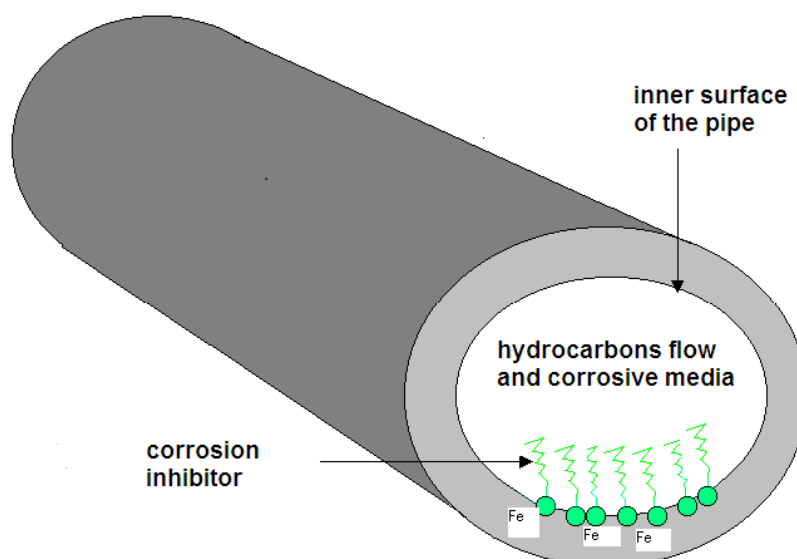


Figure 10. Representation of a CI adsorbed into a metal surface.

An inhibitor may be effective in one system, while in another it is not, (Table 1); therefore, it is convenient to consider the following factors:

- Chemical structure of the inhibitor component.
- Chemical composition of the corrosive medium.
- Nature of the metal surface.
- Operating conditions (temperature, pressure, pH, etc.).
- Thermal stability of the inhibitor. - Corrosion inhibitors have temperature limits above which lose their effectiveness because they suffer degradation of the containing components.
- Solubility of the inhibitor in the system. - The solubility of the inhibitor in the system is required to achieve optimum results in the metal surface protection; this depends on the length of the hydrocarbon chain.
- The addition of surfactants to enhance the dispersibility or solubility of inhibitors.
- Modification of the molecular structure of the inhibitor by ethoxylation to increase the polarity, and thus reach its solubility in the aqueous medium.

The main features of an inhibitor are:

- Ability to protect the metal surface.
- High activity to be used in small quantities (ppm).
- Low cost compound(s).
- Inert characteristics to avoid altering a process.
- Easy handling and storage.
- Preferably with low toxicity.
- Non-contaminant.
- It should act as an emulsifier.
- It should act as a foaming agent.

3. Experimental

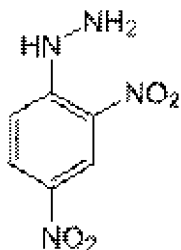
3-1 Materials:

The specimens used in this investigation were taken from aluminum with a purity of 99.99%. Rectangular aluminum specimens of size 5 cm X 1.4 cm X 0.1 cm were used for Gravimetric method and 3.2cm X 0.65 cm X 0.1 cm for Gasometry.

The name, concentration and molecular structures of the four inhibitors used were:

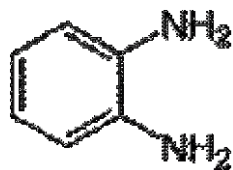
1- (2,4-Dinitrophenylhydrazine) (0.1M)

Structure:

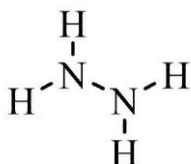


2- o-phenylenediamine (0.1 M)

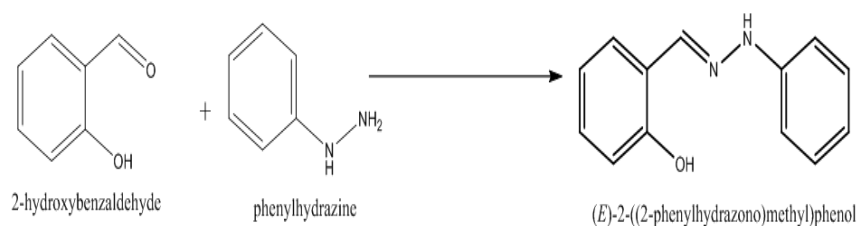
Structure:



3- Hydrazine Hydrate 80 % (0.1 M)



4- (E)-2-((2-phenylhydrazono) methyl) phenol (0.1 M)



A solution of 2M HCl was prepared by diluting concentrated acid (37% Merck) by distilled water and used as the corrosive media.

3-2 Experimental methods

3.2.1 Gravimetric measurements:

Gravimetric measurements were carried out in 50 ml of the corrosive solution. The sheets were cleaned by 4 M HCl for 1 minute, rinsed with distilled water, degreased with acetone, dried before being weighed, and then hanged in the corrosive medium. The duration time of immersion was extended up to 45 min at 298K in 1 M HCl. At the end of each experiment, the specimens were carefully washed by distilled water, dried between two filter papers and weighed. The weight loss of the metal in the corrosive solution is given by:

$$\Delta W = W_1 - W_2$$

where W_1 and W_2 are the weight of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (% IE) of the investigated inhibitor compounds was calculated from the following equations:

$$\% \text{ IE} = [1 - (\Delta W_{\text{inh}} / \Delta W_{\text{free}})] \times 100$$

where ΔW_{free} and ΔW_{inh} are weight losses of metal per unit area in the absence and presence of inhibitor in a given time period, respectively.

The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight-loss data:

$$\theta = [1 - (\Delta W_{\text{inh}} / \Delta W_{\text{free}})].$$

3.2.2 Gasometry:

The progress of the corrosion reaction was determined by volumetric measurement of the evolved hydrogen. The corrosion rate (mL. min^{-1}) was taken as the slope of the straight line representing the variation of hydrogen volume and time of exposure.

The inhibition efficiency, IE , was determined according to equation:

$$IE = [1 - (r / r_0)] \times 100$$

where r and r_0 are the corrosion rates of the aluminum specimen in the presence and absence of the used inhibitor.

The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from weight-loss data:

$$\theta = [1 - (r / r_0)].$$

3.3 Adsorption isotherm:

The adsorption isotherm can be determined by assuming that inhibition effect is due mainly to the adsorption at a metal / solution interface. Basic information on the adsorption of inhibitor on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm using the fractional surface coverage values (θ) as a function of inhibitor concentration must be obtained. The values of θ can be easily determined from the weight loss measurements by the ratio. % I.E /100, where % I.E is inhibition efficiency obtained by a weight loss method. So it is necessary to determine empirically which isotherm fits best to the adsorption of inhibitor on the Aluminium surface.

3.4. Scanning Electron Microscope

The Aluminium immersed in blank and in the inhibitor solution for a period of 45 min was removed, rinsed with double distilled water, dried and observed in a Scanning Electron Microscope to examine the surface morphology. The surface morphology measurements of the Aluminium were examined using Hitachi S-3000 computer controlled Scanning Electron Microscope.

All experiments were repeated four times and the average was taken.

4. Results and discussion.

4.1. Effect of inhibitor type:

4.1.1. **Gravimetric:** The value of percentage inhibition efficiency (% I E) and the fractional surface coverage values (θ) obtained from weight loss method for different inhibitors (0.025) in 1M HCl is summarized in Table 7 using Tables (2-6).

Table 2: Weight loss measurements for Al in 1M HCl without inhibitor.
Average weight loss with inhibitor = 0.0072 gm.

Before	After
2.6365	2.6281
2.6306	2.6262
2.6643	2.6620
2.7273	2.7136

Table 3: Weight loss measurements for Al in 1M HCl with (E)-2((2-phenylhdrazono) methyl) phenol inhibitor

Average weight loss with inhibitor = 0.0004 gm

Before	After
2.6106	2.6104
2.5041	2.5032
2.5103	2.5102
2.5913	2.5913

Table 4: Weight loss measurements for Al in 1M HCl with Hydrazine Hydrate 80 % inhibitor

Average weight loss with inhibitor = 0.0005 gm

Before	After
2.5686	2.5686
2.7800	2.7794
2.6658	2.6649
2.8049	2.8047

Table 5: Weight loss measurements for Al in 1M HCl with o-phenylenediamine inhibitor

Average weight loss with inhibitor = 0.0031 gm

Before	After
2.6456	2.6446
2.5112	2.5144
2.5224	2.5288
2.667	2.6457

Table 6: Weight loss measurements for Al in 1M HCl with 2,4-Dinitrophenylhydrazine inhibitor
Average weight loss with inhibitor = 0.10205 gm

Before	After
2.5836	2.4348
2.4647	2.3771
2.3945	2.3020
2.4855	2.4054

Table-7 Inhibition efficiency (% I E) and the fractional surface coverage values (θ) using weight loss method for Aluminium in aqueous solution of 1M HCl in the absence and presence of different inhibitors for 45 min.

Inhibitor type	(% I E)	(θ)
(E)-2((2-phenylhdrazono) methyl) phenol	94.44 %	0.94
Hydrazine Hydrate 80 %	93.05%	0.93
o-phenylenediamine	56.9 %	0.569
2,4-Dinitrophenylhydrazine	-----	-----

It is Clear from the above results that the best inhibitor was Hydrazine Hydrate 80 % and the %IE for different investigated compounds increases in the following order:

(E)-2((2-phenylhdrazono) methyl) phenol > Hydrazine Hydrate 80 % > o-phenylenediamine > 2,4-Dinitrophenylhydrazine

This is due that in case of dinitro phenyl hydrazine, the two nitro group is an electron withdrawing group that make the lone pairs of the amino group unavailable

The phenol possesses two nitrogen group which reduces the pH and more importantly, it coordinates with Al and being adsorped on its surface leading to making a protection layer on its surface which protect the Al from corrosion

Hydrazine Hydrate 80 % has two lone pair on two NH₂ not bonded with a benzene cycle as in o-phenylenediamine therefore more easily adsorped.

4.1.2. **Gasometry:** The value of percentage inhibition efficiency (% I E) and the fractional surface coverage values (θ) obtained from H₂-evolution method for **o-phenylenediamine** inhibitor as an example in 1M HCl is summarized in Table 8 using Figures11 and 12

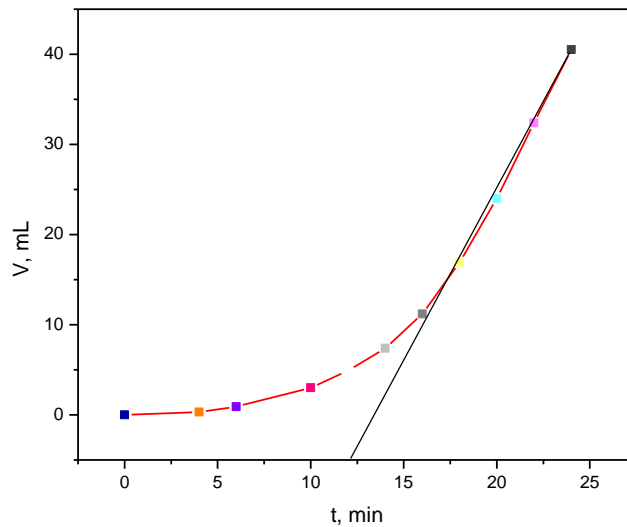


Fig. 11: Hydrogen evolution during the corrosion of aluminum in 1M HCl

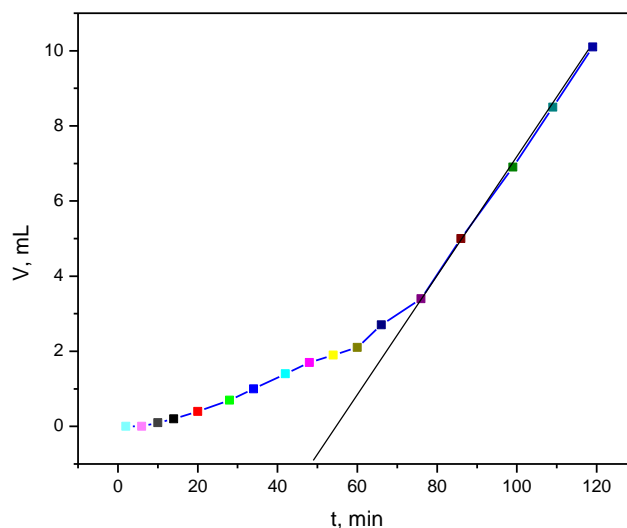


Fig12. Hydrogen evolution during the corrosion of aluminum in 1M HCl in presence of **o-phenylenediamine** inhibitor (0.10 M).

Table 8: The value of percentage inhibition efficiency (% I E) **and** the fractional surface coverage values (θ) obtained from H₂-evolution method for **o-phenylenediamine** inhibitor as an example in 1M HCl using Figures 11-12

Inhibitor type	(% I E)	(θ)
o-phenylenediamine inhibitor (0.1M)	96.1	0.961

It is Clear also from the results that the best inhibitor was Hydrazine Hydrate 80 % and the %IE for different investigated compounds increases in the following order:

.Hydrazine Hydrate 80 % > The Ligand: (E)-2((2-phenylhdrazono) methyl) phenol > o-phenylenediamine .> 2,4-Dinitrophenylhydrazine

4.2. Effect of inhibitor concentration

4.2.1. **Gravimetric:** O-phenylenediamine inhibitor as an example was used to study the effect of inhibitor concentration by weight loss method. The value of percentage inhibition efficiency (% I E) and the fractional surface coverage values (θ) obtained from weight loss method for different concentration of O-phenylenediamine inhibitor in 1M HCl is summarized in Table 13 using Tables:9-12.

It is observed from the Table 13 that the weight loss decreased, and therefore the corrosion inhibition strengthened, with an increase in inhibitor concentration. This trend may result from the fact that adsorption and surface coverage increases with the increase in concentration. Thus the surface is efficiently separated from the medium.

Table 9: Weight loss measurements for Al in 1M HCl with o-phenylenediamine (0.025 M) Inhibitor concentration
Average weight loss = 0.0023 gm

Before	After
2.4767	2.4745
2.5456	2.5432
2.6466	2.6542
2.5868	2.5846

Table 10: Weight loss measurements for Al in 1M HCl with o-phenylenediamine (0.0125 M) Inhibitor concentration
Average weight loss = 0.0048 gm

Before	After
2.5728	2.5708
2.6612	2.6584
2.7723	2.7695
2.6839	2.6819

Table 11: Weight loss measurements for Al in 1M HCl with o-phenylenediamine (0.00625M) Inhibitor concentration
Average weight loss = 0.0054 gm

Before	After
2.6500	2.6446
2.5198	2.5144
2.6309	2.6255
2.7611	2.7557

Table 12: Weight loss measurements for Al in 1M HCl with o-phenylenediamine
(0.003125 M) Inhibitor concentration
Average weight loss = 0.0061 gm

Before	After
2.6339	2.6278
2.7327	2.7266
2.7450	2.7389
2.8560	2.8499

Table 13: Inhibition efficiency (% I E) and the fractional surface coverage values (θ) using a weight loss method for Aluminium in aqueous solution of 1M HCl in the absence and presence of different concentration of O-phenylenediamine inhibitor for 45min.

Inhibitor concentration	(% I E)	(θ)
(0.025 M)	68.05 %	0.68
(0.0125 M)	33.33 %	0.33
(0.00625M)	25 %	0.25
(0.003125 M)	15.3 %	0.153

4.2.2. **Gasometry:** The value of percentage inhibition efficiency (% I E)) and the fractional surface coverage values (θ) obtained from H₂-evolution method for O-phenylenediamine inhibitor as an example in 1M HCl is summarized in Table 14 using Figures 11 and 13.

The volume of hydrogen evolved during the corrosion reaction of aluminum in 1 M HCl solutions devoid of and containing different concentrations of O-phenylenediamine is measured as a function of the reaction time, and the data are represented graphically in Fig.13 Inspection of the figure reveals that, the hydrogen evolution starts after a certain time from the immersion aluminum coupon in the test solution. It may be expected that this time corresponds to the period needed by the acid to destruct the pre-immersion oxide film before the start of the metal attack, and it is known as the incubation period. Further inspection of Fig.13 reveals linear relationship between the time of reaction and the volume of hydrogen evolved, in all of the tested solutions. However, the presence of the inhibitor decreases, markedly, the slope of the straight line. Since the slope of the line represents the corrosion reaction rate, it could be concluded that the O-phenylenediamine inhibitor has an excellent ability to inhibit the corrosion of aluminum in the acid solution. The values of IEs and the fractional surface coverage values (θ) of different concentrations of the inhibitor are given in Table 14. Inspection of Table14 reveals that the IE increases as the concentration of the inhibitor is increased.

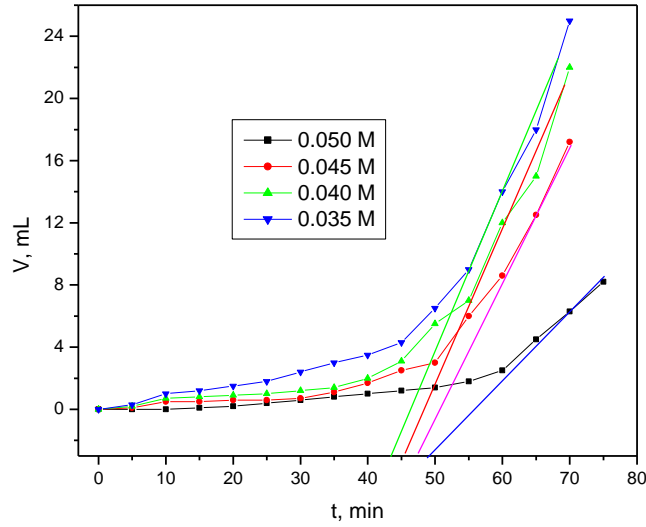


Fig13.Hydrogen evolution during corrosion of aluminum in 1M HCl containing and devoid of different concentrations O-phenylenediamine inhibitor.

Table 14: The value of percentage inhibition efficiency (% I E) and the fractional surface coverage values (θ) obtained from H₂-evolution method for different **O-phenylenediamine** inhibitor concentrations as an example in 1M HCl using Figures 11 and 13

Inhibitor concentration	(% I E)	θ
(0.050 M)	86.2	0.862
(0.045 M)	75.5	0.755
(0.040 M)	72.1	0.721
(0.035 M)	68.4	0.684

4.3. Adsorption Isotherm

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior [49]. The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated from gasometry data:

Data were tested graphically by fitting to various isotherms. A plot of $\log \theta$ vs. $\log C$ for the used inhibitor (Fig14) suggesting that the adsorption of these compounds on the Al surface follows the Freundlich adsorption isotherm which obeys the relation [50]:

$$\log \theta = \log k + n \log C \quad (0 < n < 1)$$

Plots of $\log \theta$ vs $\log C$ for adsorption of the used inhibitor on the surface of aluminum in 1M HCl is shown in Fig.14 The data gave straight lines of intercept $\log K$ and slope n indicating that Freundlich adsorption isotherm is valid for this inhibitor.

Table 15: $\log \theta$ and $\log C$ data

$\log \theta$	$\log C$
-0.06449	-1.301
-0.122	-1.347
-0.142	-1.398
-0.165	-1.456

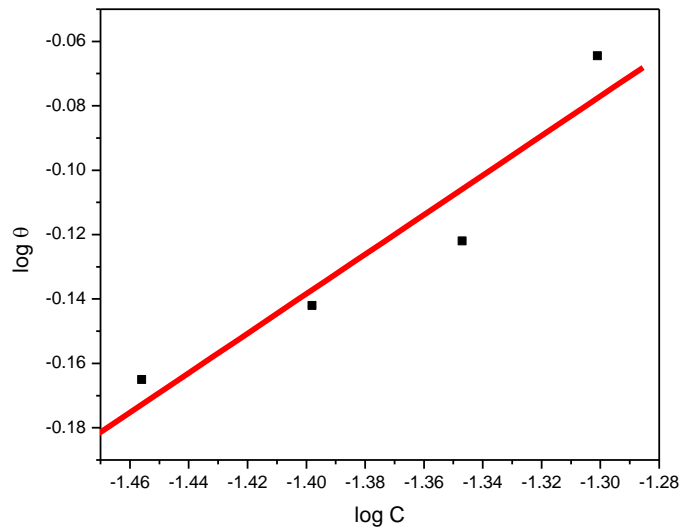


Figure 14. Curve fitting of corrosion data for aluminum in 1M HCl in presence of different concentrations of the O-phenylenediamine.inhibitor to Freundlich adsorption isotherm.

4.4. SEM analysis of metal surface:

The SEM image of magnification (x 25000) of Aluminium specimen immersed in 1M HCl for 45 min in the absence and presence of Hydrazine Hydrate 80 % inhibitor system are shown in fig.15 (a, b). The SEM micrographs of Aluminium surface in HCl without inhibitor in Fig15 (a) shows the roughness of the metal surface which indicates the corrosion of Aluminium in HCl. Fig.15 (b) indicates that in the presence of 0.05M of Hydrazine Hydrate 80 % inhibitor, the surface coverage increases, which in turn results in the formation of adsorped compound on the surface of the metal and the surface is covered by a layer of inhibitor which effectively control the dissolution of Aluminium.

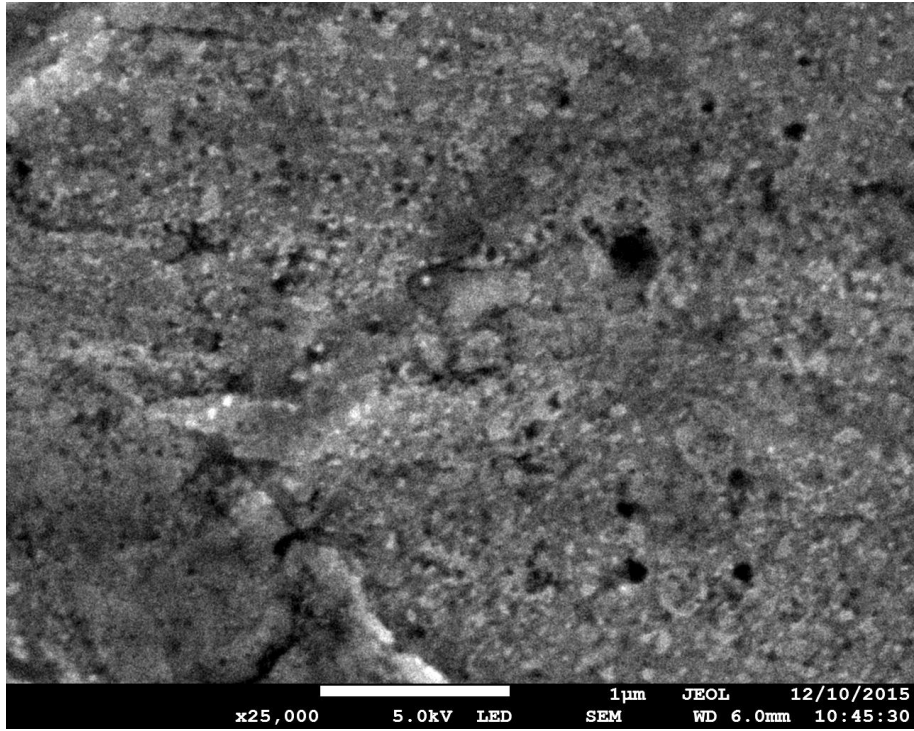


Fig15 (a) Pure Aluminium metal + 1M HCl Acid

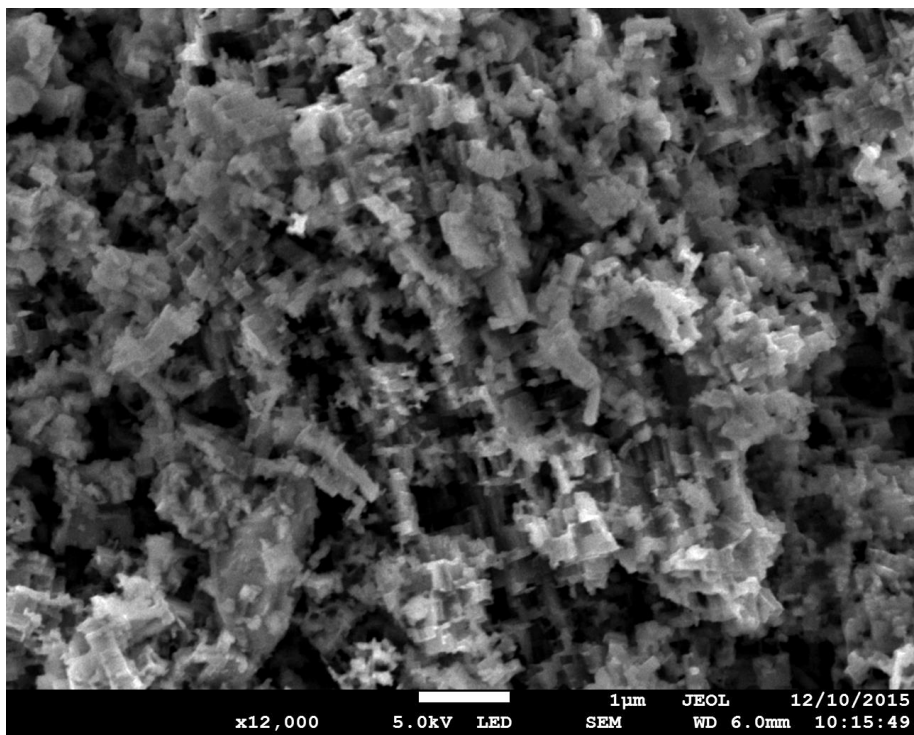


Fig 15. (b) Pure Aluminium metal + 1M HCl Acid + Inhibitor

5. CONCLUSION

On the basis of the above results the following conclusion can be drawn.

- Results obtained from the experimental data shown that Hydrazine Hydrate 80 % , o-phenylenediamine and (E)-2((2-phenylhdrazono) methyl) phenol act as effective inhibitors of corrosion in HCl acid, but 2,4-Dinitrophenylhydrazine acts as an accelerator.
- The corrosion process was inhibited by adsorption of the organic matter on the Aluminium surface. Hydrazine Hydrate 80 % , o-phenylenediamine and (E)-2((2-phenylhdrazono) methyl) phenol effectively reduced the corrosion rate of aluminium in hydrochloric acid by physically adhering to the corroding metallic surface.
- Inhibition efficiency increases with an increase in the concentration of the o-phenylenediamine.
- The adsorption of o-phenylenediamine on Aluminium surface from 1M HCl obeys the Freundlich adsorption isotherm.
- The SEM images confirm the formation of protective layer on the metal surface.
- The inhibition efficiencies obtained from gasometry and weight loss measurements are in good agreement with each other

References

- [1] Brito, P.S.D. and Sequeira, C.A.C., Organic Inhibitors of the Anode Self-Corrosion in Aluminum-Air Batteries, *Journal of Fuel Cell Science and Technology*, 2013, 11(1), 011008. DOI: 10.1115/1.4025534.
- [2] Amin M.A., Abd El-Rehim, S.S., El-Sherbini, E.E.F., Hazzazi, O.A. and Abbas, M.N., Polyacrylic acid as a corrosion inhibitor for aluminium in weakly alkaline solutions. Part I: Weight loss, polarization, impedance EFM and EDX studies, *Corrosion Science*, 2009, 51, 658-667.
- [3] Nnanna, L.A., Onwuagba, B.N., Mejeha, I.M. and Okeoma, K.B., Inhibition effects of some plant extracts on the acid corrosion of aluminium alloy, *African Journal of Pure and Applied Chemistry*, 2010, 4(1), 11-16.
- [4] Rahuma, M.N., Amer, H. and Alfergani, M., Corrosion inhibition of mild steel in 11% hydrochloric acid solutions by using black pepper (*Piper Nigrum*), *Chemical Science Transactions*, 2014, 3(2), 764-772.
- [5] Oguzie, E.E., Influence of halide ions on the inhibitive effect of congo red dye on the corrosion of mild steel in sulphuric acid solution, *Material Chemistry and Physics*, 2004, 87, 212-217.
- [6] Sharmila, A., Prema, A.A. and Sahayaraj, P.A., Influence of *Murraya koenigii* (curry leaves) extract on the corrosion inhibition of carbon steel in HCl solution, *Rasayan Journal of Chemistry*, 2010, 3(1), 74-81.
- [7] Morales-Gil, P., Walczak, M.S., Cottis, R.A., Romero, J.M. and Lindsay, R., Corrosion inhibitor binding in an acidic medium: Interaction of 2-mercaptobenzimidazole with carbon-steel in hydrochloric acid, *Corrosion Science*, 2014, 85, 109-114.
- [8] Mobin M. and Khan, M.A., Investigation on the Adsorption and Corrosion Inhibition Behavior of Gum Acacia and Synergistic Surfactants Additives on Mild Steel in 0.1 m H₂SO₄, *Journal of Dispersion Science and Technology*, 2013, DOI: 10.1080/01932691.2012.751031.
- [9] Obot, I.B., Obi-Egbedi, N.O. and Umoren, S.A., Adsorption characteristics and corrosion inhibitive properties of clotrimazole for aluminium corrosion in hydrochloric acid, *International Journal of Electrochemical Science*, 2009, 4, 863-877.
- [10] Oguzie, E.E., Okolie B.N., Ogukwe, C.E. and Unaegbu, C., Corrosion inhibition and adsorption behaviour of bismark brown dye on aluminium in sodium hydroxide solutions, *Materials Letter*, 2006, 60, 3376-3378.
- [11] Begum, A.S., Mallika, J. and Gayathri, P., Corrosion inhibition properties of some 1,3,4-thiadiazolines on mild steel in acidic medium, *Journal of Chemistry*, 2010, 7(1), 117-122.
- [12] Jeyaprabha, C., Sathiyarayanan, S., Phani, K.L.N. and Venkatachari, G., Influence of poly(aminoquinone) on corrosion inhibition of iron in acid media, *Applied Surface Science*, 2005, 252, 966-975.
- [13] Oguzie, E.E., Okolue, B.N., Ebenso, E.E., Onuoha, G.N. and Onuchukwu, A.I., Evaluation of inhibitory effect of methylene blue dye on the corrosion of aluminium in hydrochloric acid, *Material Chemistry and Physics*, 2004, 87(2/3), 394-401.
- [14] Ebenso, E.E. Ekpe, U.J. Umoren, S. Jackson, E. Abiola, O.K. Oforka, N.C. and Martinez, S., Corrosion Inhibition Studies of some plant extracts on Aluminium in acidic medium, *Journal of Corrosion Science and Technology*, 2004, (1), 96-102.

- [15] Ebenso, E.E. and Oguzie, E.E., Corrosion inhibition of mild steel in acidic media by some organic dyes, *Material Letter*, 2005, 59(17), 2163-2165.
- [16] *American Journal of Materials Science* 2014, 4(5): 194-201 DOI: 10.5923/j.materials.20140405.03
- [17] Sastri V.S. *Green Corrosion Inhibitors. Theory and Practice*. John Wiley & Sons: Hoboken, NJ; 1998.
- [18] Sastri V.S. *Corrosion Inhibitors Principles and Applications*. John Wiley & Sons: New York; 1998.
- [19] Bethencourt M. Lanthanide compounds as environmental friendly corrosion inhibitors of aluminium alloys: a review. *Corrosion Science* 1998;40(11) 1803-1819.
- [20] Olivares-Xometl O, Likhanova NV, Gómez B, Navarrete J, Llanos-Serrano ME, Arce E, Hallen JM. Electrochemical and XPS studies of decylamides of alpha-amino acids adsorption on carbon steel in acidic environment. *Applied Surface Science* 2006;252(6) 2894-2909.
- [21] Olivares-Xometl O, Likhanova NV, Domínguez-Aguilar M.A, Arce E, Dorante H, Arellanes-Lozada P. Synthesis and corrosion inhibition of alpha-amino acids alkylamides for mild steel in acidic environment. *Material Chemistry Physics* 2008;110(2-3) 344-351.
- [22] Abd El-Maksoud S.A, Fouda A.S. Some pyridine derivatives as corrosion inhibitors for carbon steel in acidic medium. *Material Chemistry Physics* 2005;93: 84-90.
- [23] Ergun Ü, Yüzer D, Emregül K.C. The inhibitory effect of bis-2,6-(3,5-dimethylpyrazolyl) pyridine on the corrosion behaviour of mild steel in HCl solution. *Material Chemistry Physics*. 2008;109: 492-499.
- [24] Noor E.A. Evaluation of inhibitive action of some quaternary N-heterocyclic compounds on the corrosion of Al-Cu alloy in hydrochloric acid. *Material Chemistry Physics*, 2009;114: 533-541.
- [25] Cruz J, Martínez-Palou R, Genesca J, García-Ochoa, E. Experimental and theoretical study of 1-(2-ethylamino)-2-methylimidazoline as an inhibitor of carbon steel corrosion in acid media. *Journal of Electroanalytical Chemistry* 2004;566(1) 111-121.
- [26] Martínez-Palou R, Rivera J, Zepeda L.G, Rodríguez A.N, Hernandez M.A, Marín-Cruz J, Estrada A. Evaluation of corrosion inhibitors synthesized from fatty acids and fatty alcohols isolated from sugar cane wax. *Corrosion* 2004;60(5) 465-470.
- [27] Olivares-Xometl O, Likhanova NV, Martínez-Palou R, Domínguez-Aguilar MA. Electrochemistry and XPS study of an imidazoline as corrosion inhibitor of mild steel in an acidic environment. *Materials and Corrosion* 2009;60(1) 14-21.
- [28] Liu F.G, D.u. M, Zhang J, Qiu M. Electrochemical behavior of Q235 steel in saltwater saturated with carbon dioxide based on new imidazoline derivative inhibitor. *Corrosion Science* 2009; 51(1) 102-109.
- [29] Likhanova N.V, Martínez-Palou R, Veloz M.A, Matías D.J, Reyes-Cruz VE, Olivares-Xometl O. Microwave-assisted synthesis of 2-(2-pyridyl)azoles. Study of their corrosion inhibiting properties. *Journal of Heterocyclic Chemistry* 2007; 44(1) 145-153.
- [30] Popova A, Christov M, Zwetanova A. Effect of the molecular structure on the inhibitor properties of azoles on mild steel corrosion in 1 M hydrochloric acid. *Corrosion Science* 2007; 49(5) 2131-2143.
- [31] Antonijevic M.M, Milic S.M, Petrovic M.B. Films formed on copper surface in chloride media in the presence of azoles. *Corrosion Science* 2009; 51(6) 1228-1237.

- [32] Tallman D.E, Spinks G, Dominis A, Wallace G.G. Electroactive conducting polymers for corrosion control Part 1. General introduction and a review of non-ferrous metals. *Journal of Solid States Electrochemistry* 2002; 6(2) 73-84. b) Spinks G, Dominis A, Wallace GG, Tallman DE. Electroactive conducting polymers for corrosion control -Part 2. Ferrous metals. *Journal of Solid States Electrochemistry* 2002; 6(2) 85-100.
- [33] *Chemical Inhibitors for Corrosion Control*. The Royal Society of Chemistry; 1990.
- [34] *The Multimedia Corrosion Guide [CD-ROM]*. INSA, Lyon; 2013.
- [35] Marcus P, Maurice V, Strehblow H.H. Localized corrosion (pitting): A model of passivity breakdown including the role of the oxide layer nanostructure. *Corrosion Science*, 2008; 50(9) 2698-2704.
- [36] Levy A.V. The erosion-corrosion behavior of protective coatings. *Surface and Coatings Technology*. 2002; 36(1-2) 387-406.
- [37] Sieradzki K, Newman RC. Stress-corrosion cracking. *Journal of Physics and Chemistry of Solids*. 1987; 48(11) 1101-1113.
- [38] Song G, Johannesson B, Hapugoda S, StJohn D. Galvanic corrosion of magnesium alloy AZ91D in contact with an aluminium alloy, steel and zinc. *Corrosion Science*, 2004; 46(4) 955-977.
- [39] Al-Hashem A, Riad W. The role of microstructure of nickel–aluminium–bronze alloy on its cavitation corrosion behavior in natural seawater. *Material Characterization*, 2002; 48(1) 37-41. b) Neville A, McDougall BAB. Erosion-and cavitation-corrosion of titanium and its alloys. *Wear* 2001 ;250(1-12) 726-735.
- [40] González J.L, Ramirez R, Hallen J.M, Guzman R.A. Hydrogen-Induced Crack Growth Rate in Steel Plates Exposed to Sour Environments. *Corrosion* 1997; 53(12) 935-943.
- [41] Revie W, Uhlig H.H. *Corrosion and corrosion control: An introduction to corrosion science and engineering*. Wiley-Interscience: NewYork; 2008. <https://www.corrosioncost.com> (accessed 1 august 2013), Ref. 2, p537-566.
- [42] Distasio JI. *Chemical for Oil Field Operations*. Ed. Noyes Data Corp., New Jersey, E.U; 1981.
- [43] Salensky G. Organic Corrosion Inhibitors. In: Salensky, G. (ed.) *Handbook of Coatings Additives*; 1987. p340-356. Ref. 2, p681-688.
- [44] *Corrosion Mechanisms in Theory and Practice*, 3rd Ed. Marcus P (Ed.), Taylor and Francis Group, CRC, Boca Raton; 2012. Ref. 2, p885-894.
- [45] Chen G, Zhang M, Zhao J, Zhou R, Meng Z, Zhang Z. Investigation of Ginkgo biloba leave extracts as corrosion and oil field microorganism inhibitors. *Chemistry Central Journal* 2013; 7(Article Number: 83).
- [46] Okafor P.O, Ikpi M.E, Uwah I.E, Ebenso E.E, Ekpe U.J, Umoren S.A. Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media. *Corrosion Science* 2008; 50(8) 2310-2317.
- [47] Umoren S.A, Ekanem U.F. Inhibition of Mild Steel Corrosion in H₂SO₄ using Exudate Gum from *Pachylobus Edulis* and synergistic Potassium Halides Additives. *Chemical Engineering Communications* 2010 ;197(10) 1339-1356.
- [48] Rafael Martinez Palou, Octavio Olivares-Xomelt and Natalya V. Likhanova Additional information is available at the end of the chapter <http://dx.doi.org/10.5772/57252>

- [49] E. E. Oguzie, "Corrosion inhibition of aluminium in acidic and alkaline media by *Sansevieria trifasciata* extract," *Corrosion Science*, vol. 49, no. 3, pp. 1527–1539, 2007.
- [50] M. Kliskic, J. Radosevic, S. Gudic and V. Katalinik, Aqueous extract of *Rosmarinus officinalis* L. as inhibitor of Al-Mg alloy corrosion in chloride solution. *J. Appl. Electrochem.*, 30(2000)823.