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Corrosion inhibition of aluminum in different media using environmentally friendly inhibitors

A graduation research project

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ABSTRACT

Inhibition of Aluminum corrosion in 2M hydrochloric acid solution using different inhibitors has been studied by weight loss and hydrogen evolution measurement. It was found that Honey, Hibiscus and Mint act as good inhibitors for aluminum corrosion in the acid solution and the best one was **Mint**. The inhibitory action of the used inhibitors in 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 due to the presence of lone pair on oxygen. The inhibition efficiencies obtained from gasometry and weight loss measurements are in good agreement with each other

ملخص

تم دراسة تثبيط تآكل الألومنيوم في 2 M من حمض الهيدروكلوريك باستخدام مثبطات مختلفة و بطرق حكم مختلفة و هي طريقة فقدان الوزن وطريقة قياس تصاعد الهيدروجين. وقد تبين أن:

الكرديه والنناع,العسل

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

النناع

ونوقشت ميكانيكية التثبيط للمثبطات المستخدمة من وجهة نظر إدمصاص المثبط على أسطح الألومنيوم. وقد وجد أن ادمصاص هذه المركبات على سطح الألومنيوم بسبب وجود زوج الألكترونات على الأكسجين. ووجد أن كفاءات التثبيط التي تم الحصول عليها من قياسات تصاعد الغاز وفقدان الوزن هي في اتفاق جيد مع بعضها البعض.

CHAPTER 1 INTRODUCTION

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 [1,2]. 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 2M hydrochloric acid using different inhibitors. It will be study the corrosion using weight loss method and the method of measuring hydrogen evolution method.

CHAPTER 2 LITTERATURE 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. 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_3^-), 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 [33].

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 .

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.

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 . [34].

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 ; these areas are the most susceptible to the corrosion process [35].

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. 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].

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 [37].

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 .[38].

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 .[39].

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. 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.

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 .

- b.** With corrosimetric specimens. These probes are installed at the places to be monitored. A corrosometer 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 CIs 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 1).

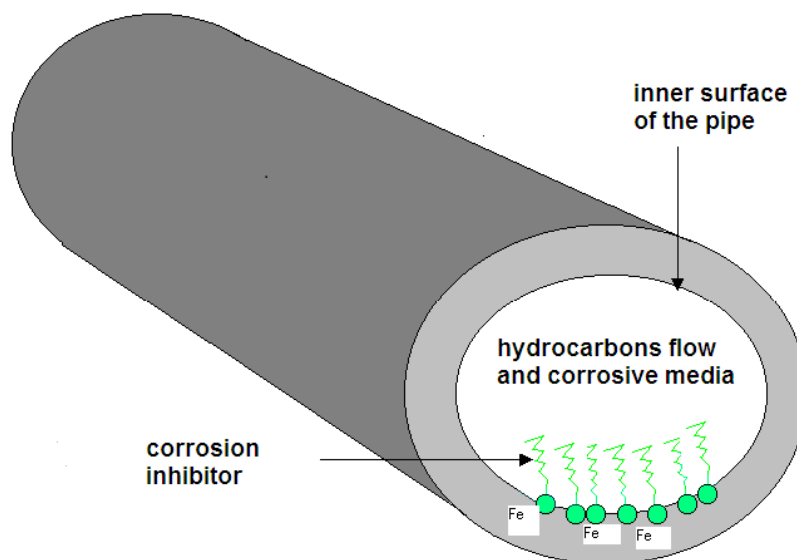


Figure 1. Representation of a CI adsorbed into a metal surface.

An inhibitor may be effective in one system, while in another it is not; 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.

2.5 Environmentally Friendly Corrosion Inhibitors (EFCIs)

In recent years, owing to the growing interest and attention of the world towards the protection of the environment and the hazardous effects of using chemicals on the ecological balance, the traditional approach on CIs has gradually changed. As mentioned before, for an inhibitor to be an effective protector against metal corrosion, it should be readily adsorbed on the metal surface through either physisorption or chemisorption processes. Either of these adsorption processes depends primarily on the physicochemical properties of the inhibitor group such as functional groups, electronic density at the donor atom, molecular structure, etc. For instance, organic molecules, which have had a wide applicability and that have been extensively studied and used as CIs, often contain nitrogen, oxygen, and sulfur atoms, as well as multiple bonds in their molecules.

2.5.1 Evaluating the toxicity of CIs

Aspects to be taken into account in the development of CIs are their toxicity and impact on environmental pollution of both the active and other components of the formulation. The European Economic Community assigned the Paris Commission (PARCOM) the task of providing guidance for environmental pollution control, protection of the ecosystems and the evaluation of the toxicity of raw materials and industrial waste products. The PARCOM Environmental has developed a standardized test that covers three aspects:

1. Toxicity: This must be determined for the formulation as a whole. Toxicity should be measured by using either the 50 Lethal Concentration (LC50), which is the concentration at which 50% of the test organisms are killed, or the EC50, which is the concentration that can cause an adverse organism affection, e.g. the concentration decreases the emission intensity of luminescent bacteria by 50% or the concentration decreases the growth or average weight of certain microorganisms by 50%.

2. Biodegradation: It must be determined for all the formulation components. This test measures the persistence in the environment of the formulation components. The allowable limit is more than 60% after 28 days.

3. Bioaccumulation: This test measures the level of product buildup in the body. Bioaccumulation is measured by the partition coefficient.

This means that the greater the partition coefficient, the more likely it is that the compound passes through the cell membrane, being bioaccumulated. EFCIs can be arbitrarily divided into two categories: natural products and low toxicity synthetic products. In this last category, special attention has been paid to a new class of low toxicity organic compounds known as ionic liquids. There are a few studies where CIs are evaluated according to the methodology described in this section and designed as low toxicity CIs or EFCIs. Most of the inhibitors that receive this rating are based on products that are derived from natural sources that are considered as compatible,

biodegradable or environmentally friendly, although strictly, their toxicity has not been assessed by following the testing protocol presented above. Recent research works on the study of EFCIs with particular interest in those with potential applications in the Petroleum Industry is given.

2.5.2 Natural products as EFCIs

Natural products have been studied extensively as corrosion inhibitors both in product mixtures extracted from natural sources such as plants or essentially pure products derived from animals or plants (i.e. vitamins and aminoacids). From the economic and environmental viewpoints, plant extracts are an excellent alternative as inhibitors because of their availability and biodegradability. These extracts can be obtained in a simple way and purification methods are not required. The extracts are generally obtained from cheap solvents that are widely available, at a low cost and with low toxicity; the aqueous extract is more relieved, but due to the low solubility of many natural products in water, common ethanol extracts are also obtained. These extracts contain a variety of natural products such as essential oils, tannins, pigments, steroids, terpenes, flavones and flavonoids, among other well-known active substances used as CIs. In general, these compounds present conjugated aromatic structures, long aliphatic chains such as nitrogen, sulfur, and oxygen heteroatoms with free electron pairs that are available to form bonds with the metal surface; in most cases, they act synergistically to exhibit good efficiency regarding the corrosion protection. This can be demonstrated in the case of *Ginkgo biloba* in which the main components (flavonoids and terpenoids) have been identified. This extract has demonstrated excellent efficiency as CI with potential applications in the Oil Industry concerning the corrosion inhibition of Q235A steel. The antibacterial activity of the extracts against oil field microorganisms (SRB, IB and TGB) has also been proved [49].

The main disadvantage of using plant materials as CIs is their frequently low stability, they are readily biodegradable; however, this disadvantage can be minimized or avoided by adding biocides such as *N*-cetyl-*N,N,N*-trimethyl ammonium bromide. In the last years, Umoren and Obot's research group has published several papers about the evaluations of plant extracts as CIs, for example, *Phyllanthus amarus* [50], *Pachylobus edulis* [51], *Raphia hookeri* [52], *Ipomoea involcrata* [53] and *Spondias mombin L.* [54]. Recently, this group described the inhibitive action of ethanolic extracts from leaves of *Chlomolaena Odorata L.* (LECO) as eco-friendly CI of acid corrosion of aluminum in 2 M HCl, using hydrogen evolution and thermometric techniques [55]; and more recently, for corrosion of mild steel in H₂SO₄ solutions [56]. In this last paper, the obtained results showed that LECO functioned as a CI and its efficacy increased with the extract concentration, but decreased with temperature. At a concentration as low as 5 %v/v of the extract, the inhibitory efficiency reached about 95% at 303 K, and 89% at 333 K. In another interesting work, this group showed the excellent inhibitory properties of Coconut coir dust extract (CCDE) as a corrosion inhibitor of aluminum in 1 M HCl, using weight loss and hydrogen evolution techniques at 30 and 60°C by monitoring the volume of evolved hydrogen gas at fixed time intervals. The representative plots of the volume of the evolved hydrogen gas as a function of the reaction time at 30 and 60°C for Al in 1 M HCl, in the absence and presence of different concentrations of the CCDE, showed a remarkable increase in the volume of evolved H₂ gas in the blank acid solution at both studied temperatures. As for the introduction of CCDE into the corrosive medium, it

is seen that there is a considerable reduction in the volume of evolved hydrogen gas, suggesting that the CCDE components were adsorbed onto the metal surface, and blocked the electrochemical reaction efficiently by decreasing the available surface area [57].

In the category of natural isolated products, aminoacids and their derivatives are some of the most studied pure compounds as EFCI. These natural compounds and derivatives have been used as good CIs for mild steel aluminum [58], and alloys [59] and [60] in different aggressive solutions. Very recently, the inhibitory properties of l-histidine on the corrosion of carbon steel in weak acid media containing acetic acid/sodium acetate have been tested. The inhibition efficiencies obtained by weight loss measurements are in good agreement with values given by the Tafel method and electrochemical impedance spectroscopy. The adsorption of l-histidine obeys the Langmuir isotherm; the negative values of the Gibbs energy indicate the nature of the interactions between the inhibitor molecules and metal surface. Further, the inhibitory effect was studied by using scanning electron microscopy and energy dispersive X-ray analysis [61].

The using of as corrosion inhibitors are very little especially with Al in the literatures [62-65] therefore this project focused for these inhibitors.

3. Experimental

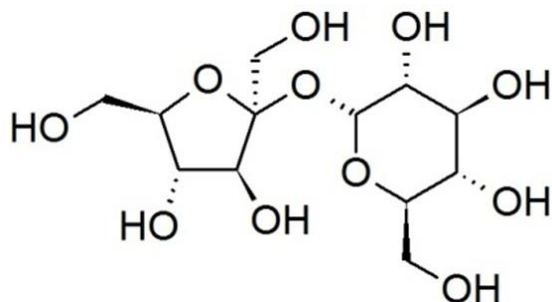
3-1 Materials:

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 0.14 cm were used for Gravimetric method and 3.2cm X 0.65 cm X 0.14 cm for Gasometry.

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

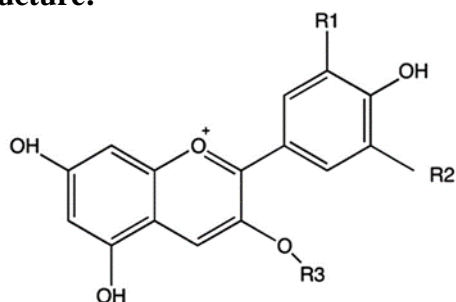
1- Honey (1g/L)

Structure:



2- Hibiscus (2.5g/1L)

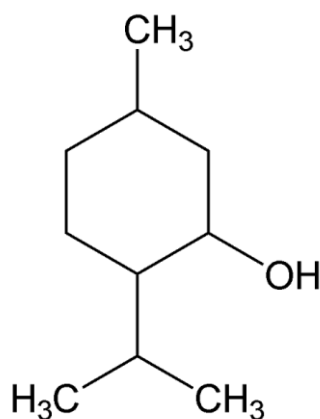
Structure:



Cyanidin-3-sambubioside (R1= OH; R2= H; R3= Sambubioside)
 Delphinidin-3-sambubioside (R1= OH; R2= OH; R3= Sambubioside)
 Cyanidin-3-glucoside (R1= OH; R2= H; R3= Glucose)
 Delphinidin-3-glucoside (R1= OH; R2= OH; R3= Glucose)

2- Mint(2.5g/1L)

Structure:



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 5 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 2 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 ($\text{mL} \cdot \text{min}^{-1}$) 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. $\% \text{ IE} / 100$, where $\% \text{ IE}$ 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.

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 in 2M HCl is summarized in Table 5 using Tables (1-4).

Table 1: Weight loss measurements for Al in 2M HCl without inhibitor.
Average weight loss without inhibitor = 0.0648 g.

Before	After
2.5550	2.4914
2.5058	2.4403
2.7345	2.6766
2.7249	2.7028

Table 2: Weight loss measurements for Al in 2M HCl with Honey inhibitor
Average weight loss with inhibitor = 0.0161 g

Before	After
2.5150	2.5002
2.6405	2.6256
2.6414	2.6202
2.5982	2.5847

Table 3: Weight loss measurements for Al in 2M HCl with Hibiscus inhibitor
Average weight loss with inhibitor = 0.00335 g

Before	After
2.6952	2.6934
2.6356	2.6316
2.6173	2.6129
2.6616	2.6584

Table 4: Weight loss measurements for Al in 2M HCl with Ment inhibitor
Average weight loss with inhibitor = 0.00113 g

Before	After
2.5691	2.5675
2.6931	2.6923
2.6338	2.6329
2.5899	2.5887

Table-5 Inhibition efficiency (% I E) and the fractional surface coverage values (θ) using weight loss method for Aluminium in aqueous solution of 2M HCl in the absence and presence of different inhibitors for 45 min.

Inhibitor type	(% I E)	(θ)
Honey	75.2 %	0.75
Hibiscus	94.8%	0.95
Mint	98.3 %	0.98

It is clear from the above results that the best inhibitor was Mint and the %IE for different investigated compounds increases in the following order:

Mint > Hibiscus > Honey

The inhibitive action of the inhibitors was attributed to the adsorption of its components to the Al surface. The reduction in the corrosion rate was due to the presence of groups which contains from heteroatoms (oxygen and carbon), blocking the active sites on the metal. Also, in the case of honey and hibiscus hydroxyl groups are more acidic and the presence of common ion effect and the absence of groups of electrons giving rise effect of H^+ . In mint condition hydroxyl group be more base because the presence of alkyl groups gives electron rich minimizing the impact of H^+ .

4.1.2. **Gasometry:** The value of percentage inhibition efficiency (% I E) **and** the fractional surface coverage values (θ) obtained from H_2 -evolution method for **Mint** inhibitor as an example in 2M HCl is summarized in Table 6 using Figures 2 and 3

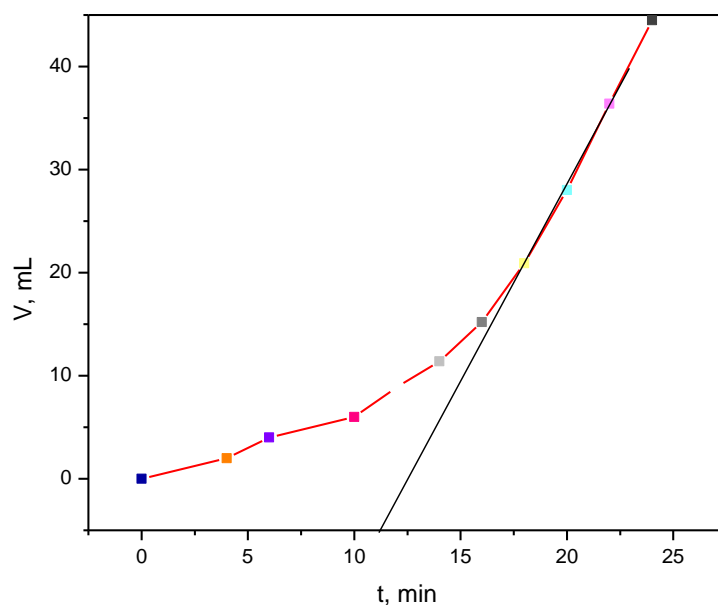


Fig. 2: Hydrogen evolution during the corrosion of aluminum in 2M HCl

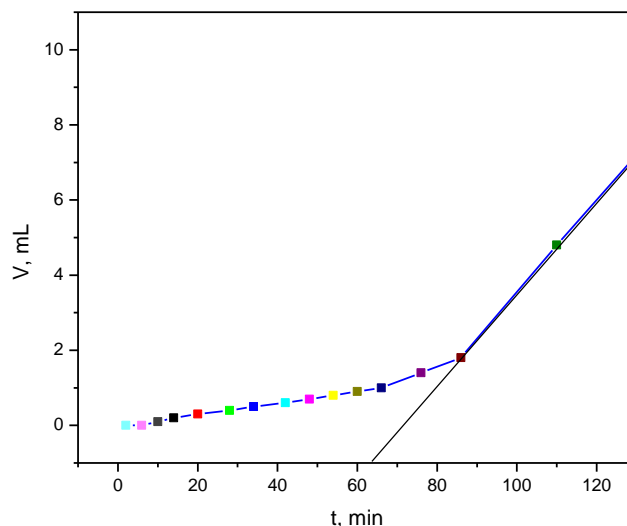


Fig3. Hydrogen evolution during the corrosion of aluminum in 2M HCl in presence of **Mint** inhibitor (5g/1L).

Table 6: The value of percentage inhibition efficiency (% I E) **and** the fractional surface coverage values (θ) obtained from H₂-evolution method for **Mint** inhibitor as an example in 2M HCl using Figures2-3.

Inhibitor type	(% I E)	(θ)
Mint inhibitor (2.5g/L)	96.6	0.97

It is clear also from the results that the best inhibitor was Mint and the %IE for different investigated compounds increases in the following order:

$$\text{Mint} > \text{Hibiscus} > \text{Honey}$$

5. CONCLUSION

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

- Results obtained from the experimental data shown that Honey, Hibiscus and Mint act as effective inhibitors of corrosion in 2M HCl acid for Al.
- The corrosion process was inhibited by adsorption of the organic matter on the Aluminium surface. Honey, Hibiscus and Mint effectively reduced the corrosion rate of aluminium in hydrochloric acid by physically adhering to the corroding metallic surface.
- The inhibition efficiencies obtained from gasometry and weight loss measurements are in good agreement with each other.

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