



Sudan University of Science and Technology
College of Graduate Studies



**Corrosion of Copper and a copper alloy in different
aqueous media**

تآكل النحاس وسبيكة النحاس في أوساط مائية مختلفة

**A Thesis Submitted in Partial Fulfillment for the
Requirements of the Degree of M.Sc in Chemistry**

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آية

بسم الله الرحمن الرحيم

قال تعالى :

﴿اللَّهُ نُورُ السَّمَوَاتِ وَالْأَرْضِ مِثْلُ نُورِهِ كَمِشْكُوتٍ فِيهَا مِصْبَاحٌ الْمِصْبَاحُ فِي زُجَاجَةٍ
الزُّجَاجَةُ كَأَنَّهَا كَوْكَبٌ دُرِّيٌّ يُوقَدُ مِنْ شَجَرَةٍ مُبَارَكَةٍ زَيْتُونَةٍ لَا شَرْقِيَّةٍ وَلَا غَرْبِيَّةٍ يَكَادُ
زَيْتُهَا يُضِيءُ وَلَوْ لَمْ تَمْسَسْهُ نَارٌ نُورٌ عَلَى نُورٍ يَهْدِي اللَّهُ لِنُورِهِ مَنْ يَشَاءُ وَيَضْرِبُ
اللَّهُ الْأَمْثَلَ لِلنَّاسِ وَاللَّهُ بِكُلِّ شَيْءٍ عَلِيمٌ﴾

صدق الله العظيم

سورة النور الآية (35)

Dedication

I dedicate this research to my parents, my husband, my children, my brothers and sisters.

Acknowledgement

My great thanks are due to Allah, Almighty.

Special thanks to Dr. Mohammed Sulieman Ali for his help and guidance throughout this work.

also great thanks are due to my family .

Abstract

In this research, the corrosion behavior of the copper and copper alloy in different conditions and environment were studied. The corrosion behaviour and mechanism for copper and copper alloy in(HNO_3 , H_2SO_4 , HCl , NaCl) solutions were studied by chemical mass loss, kinetic of corrosion, half life time, inhibitor efficiency and corrosion rate of inhibitor efficiency methods at 25°C . were also investigated. The chemical results revealed that copper and copper alloy corrodes in(HNO_3 , H_2SO_4 , HCl , NaCl) solutions the corrosion rate increased with the increasing in acid concentration. Weight loss technique were used to study the corrosion inhibition efficiency in 1.0 M(HNO_3 , H_2SO_4 , HCl , NaCl) solutions by using the urea and acetanilide. The results showed that urea is good corrosion inhibitors, Corrosion inhibition efficiency increased with increasing weight of inhibitor. Inhibition efficiency was found maximum up to 68.5% for copper. The rate of metal dissolution increases with acid concentration. The corrosion of copper was found to be greater than copper alloy .

المستخلص

التآكل عباره عن سلاسل معقده من التفاعلات بين مختلف الظروف البيئيه و سطح المعدن.السبب الاساسي لتدهور المعادن هو التآكل الخارجي المتضمن بواسطة البيئه وظروف العمليات. اختيار المعدن يعتمد على عدد من العوامل تتضمن سلوكه تجاه التآكل في هذا البحثتمت دراسة سلوك النحاسوسبيكة من النحاس تجاه التآكل في محاليل مائية مختلفة. تمت دراسة سلوك النحاس وسبيكة من النحاس تجاه التآكل بواسطة نصف العمر,فقد الكتله ,التآكل الحركي,كفاءة المثبط الميكانيكية في وجود محاليل HNO_3 , HCl , $NaCl$, H_2SO_4 وكذلك معدل كفاءة المثبط عند درجة حرارة الغرفة . النتائج الكيميائية بعد غمر النحاس في هذه المحاليل المائية أظهرت أن معدل التآكل يزيد بزيادة تركيز الحامض . وتقنية فقد الوزن استخدمت لدراسة كفاءة مثبط التآكل (اليوريا والاستانليد) في هذه المحاليل عند تركيز 0.1 مولاري وجد ان اليوريا افضل مثبط للتآكل مقارنة بالاستانليد.كفاءة المثبط ايضا تزيد بزيادة وزن المثبط. اعلي نسبة كفاءة هي 68.5% للنحاس.وجد ان تآكل النحاس في المحاليل السابقة اكبر من تآكل سبيكة النحاس.

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Chapter one

Introduction and Literature Review

Chapter one

Introduction and Literature Review

1- Introduction

1.1 Definition of corrosion:

Corrosion is the destructive attack of a material by reaction with its environment^(1,2). Corrosion is the destructive attack of a metal and its properties by chemical (dry corrosion) or electrochemical (wet corrosion) reaction with its environment⁽³⁾. Corrosion is an electrochemical process that involves the rearrangement of electrons between metal surface and an aqueous electrolytic solution. Corrosion is considered as the destructive disintegration of a metal by electrochemical means in which a metal is destroyed by a chemical reaction⁽⁴⁾.

1.2 Cost of corrosion:

The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product, reduction in efficiency, costly maintenance, and expensive overdesign; it also jeopardizes safety and inhibits technological progress⁽¹⁾. Economic costs. Corrosion can increase the operating expenses of a water distribution system. For example, when iron mains build up with tuberculation, flow rates and efficiency are reduced. This could lead to the premature replacement of mains. Fortunately, this kind of corrosion is easily seen and identified. Health costs. Corrosive water can cause the leaching of lead and copper into a water supply. Unfortunately, lead leaching problems are not as visible as other types of corrosion problems. To determine lead leaching, the water must be tested for the presence of lead⁽⁵⁾.

1.3 Forms of corrosion:

Corrosion damage can occur in many ways, for example, in failure by cracking, loss of strength, etc. Forms of corrosion are uniform attack, galvanic corrosion, selective leaching, erosion corrosion, stress corrosion, crevice corrosion, pitting and intergranular corrosion⁽³⁾.

1.3.1 Uniform attack:

Uniform corrosion is the attack of a metal at essentially the same at all exposed areas of its surface⁽³⁾.

1.3.2 Galvanic Corrosion:

Galvanic corrosion tends to occur when dissimilar conducting materials are connected electrically and exposed to an electrolyte^(3,6).

1.3.2.1 Factors in galvanic corrosion:

Many factors play a role in galvanic corrosion in addition to the potential difference between the two coupled metals. Depending on the circumstances, some or all of the factors illustrated in Figure 1 may be involved. Generally, for a given couple, the factors in categories (a)–(c) vary less from one situation to another than the factors in categories (d)–(g). Effects of geometric factors on galvanic actions can, in many cases, be mathematically analyzed. On the other hand, effects of electrode surface conditions on reaction kinetics in real situations can be very difficult to determine. Compared to normal corrosion, galvanic corrosion is generally more complex because, in addition to material and environmental factors, it involves geometrical factors⁽⁶⁾.

1.3.2.2 Material Factors:

1.3.2.2.1 Effects of Coupled Materials

As listed in Figure 1, all the factors affecting the electrode properties, such as those under categories (a)–(g), have an influence on galvanic action between any two metals. The reversible electrode potentials of the two coupled metals determine the intrinsic polarity of a galvanic couple, whereas the reactions, metallurgical factors, and surface conditions determine the actual polarity under a given situation because the actual potential (the corrosion potential) of a metal in an electrolyte is usually very different from its thermodynamic equilibrium value due to kinetic processes⁽⁶⁾.

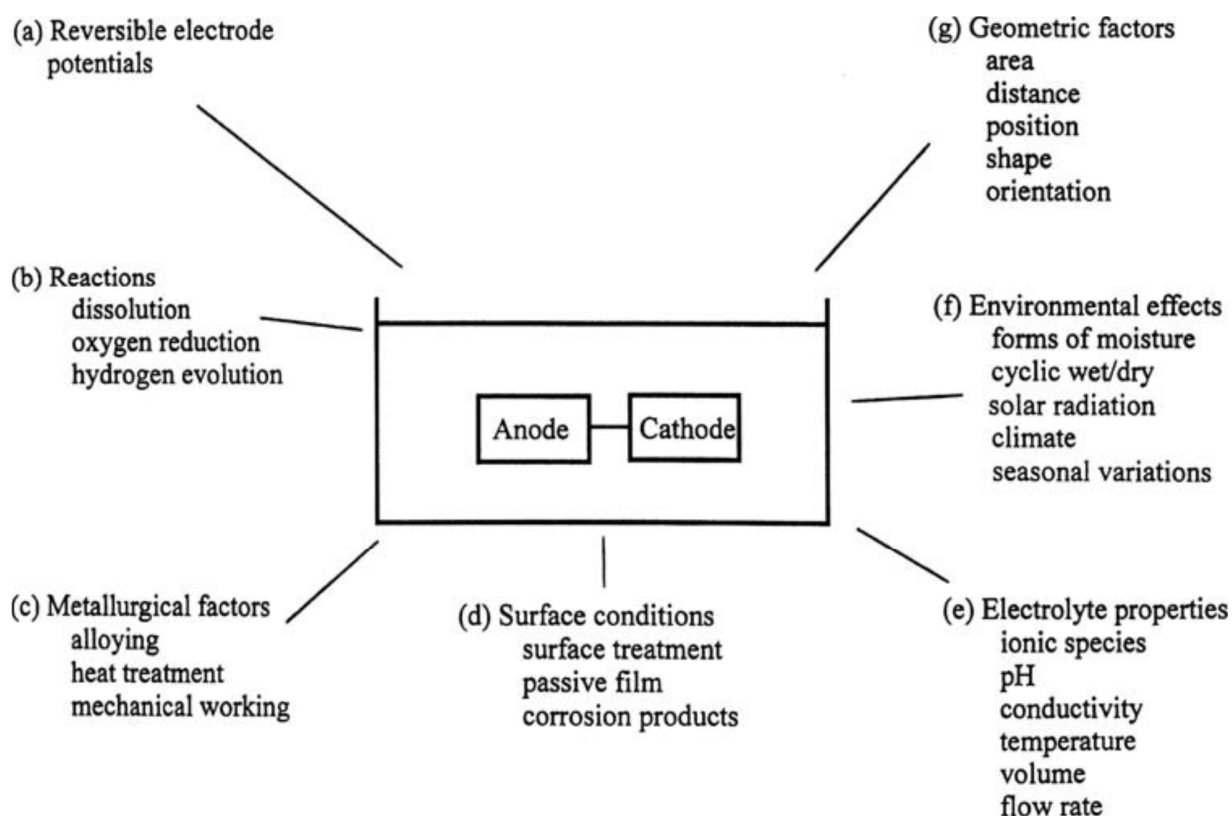


Figure1.1 Factors involved in galvanic corrosion of bimetallic couple.

1.3.2.2.2 Effect of Area:

The effect of anode and cathode areas on galvanic corrosion depends on the type of control in the system, as illustrated later in Figure 1.1. If the galvanic system is under cathodic control, variation in the anode area has little effect on the total rate of corrosion, but variation of the cathode area has a significant effect. The opposite is true if the system is under anodic control⁽⁶⁾.

1.3.2.2.3 Effect of Surface Condition:

The surface of metals in contact with an electrolyte is generally not “bare” but is covered with a surface layer, at least an adsorption layer, but often a solid surface film. This is the most important factor that causes the difference between the intrinsic polarity and apparent polarity and between the difference in potentials and the extent of galvanic corrosion. Formation of a surface film, whether a salt film or an oxide film, may significantly change the electrochemical properties of the metal surfaces, resulting in very different galvanic action⁽⁶⁾.

1.3.3 Crevice Corrosion:

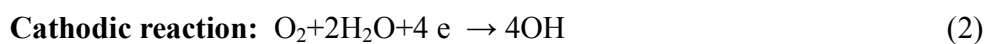
Crevice corrosion is a localized form of corrosive attack. Crevice corrosion occurs at narrow openings or spaces between two metal surfaces or between metals and nonmetals⁽³⁾. Crevice corrosion is a type of localized corrosion that can be found within crevices or at shielded surfaces where a stagnant solution is present. It is one of the most frequently encountered forms of localized corrosion and at the same time one of the most harmful ones because it happens in the alloys that normally exhibit perfect corrosion resistance⁽⁷⁾.

1.3.3.1 Theory of Crevice Corrosion:

Corrosion requires energy. During corrosion the reacting components go from a higher to a lower energy state and release the energy needed for the reaction. In the dry corrosion the metal and the oxygen combine to produce the oxide on the surface because the reaction leads to a compound (the oxide) at a lower energy level. The oxide layer shields the metal from the oxygen and forms a barrier. The oxide will not react with the oxygen in the air or the metal⁽⁷⁾.

1.3.3.2 Mechanism:

The Fontana and Greene model describes crevice corrosion mechanism. This model consists of four stages. Stage 1: Corrosion occurs as normal both inside and outside the crevice:



The positively charged metallic ions are electrostatically counterbalanced by OH^- . Stage 2: at this stage, the cathodic reaction inside the crevice consumed most of the oxygen available. Stage 3: Cl^- and OH^- diffuse into the crevice to maintain a minimum potential energy. Metal chloride is formed. Hydrolysis of metal chloride lowers pH. Stage 4: More Mn^{+} ions attack more Cl^- leads to lower pH inside crevice, metal dissolution accelerates and more Mn^{+} ions will be produced that will lower pH⁽⁷⁾.

1.3.3.3 Prevention Methods:

The simplest method for preventing crevice corrosion is reducing crevices in the design of the Structure⁽⁷⁾.

1.3.4 Pitting:

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Pitting corrosion can produce pits with their mouth open (uncovered) or covered with a semi-permeable membrane of corrosion products. Pits can be either hemispherical or cup-shaped ⁽³⁾.

1.3.5 Intergranular corrosion:

Intergranular corrosion is very relevant for the brewery industry. It consists of a localized attack, where a narrow path is corroded out preferentially along grain boundaries of a metal. This type of corrosion may have extreme effects on mechanical properties, resulting in a loss of strength and ductility⁽³⁾.

1.3.6 Selective leaching:

It is also known as "parting" or "dealloying" is the selective removal of one element from an alloy leaving an altered residual structure⁽³⁾.

1.3.7 Erosion corrosion:

Erosion corrosion is the acceleration or increase in the rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface⁽³⁾.

1.3.8 Stress corrosion:

Stress corrosion cracking (SCC) refers to the cracking caused by the simultaneous presence of tensile stress and a corrosive environment. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material⁽³⁾.

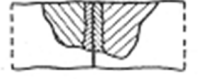
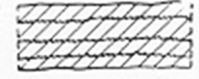
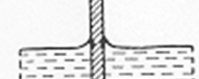
 Uniform corrosion The reaction starts at the surface and proceeds uniformly.	 Localized corrosion (pitting corrosion) The basis metal is eaten away and perforated in places in the manner of holes, the rest of the surface being affected only slightly or not at all.	 Wide pitting corrosion The corrosion causes localized scarring.
 Intergranular corrosion Imperceptible or barely perceptible from outside, since the corrosion proceeds at the grain boundaries.	 Transgranular or intragranular corrosion The grain boundary material is retained, since the corrosion proceeds preferentially within the grain.	 Galvanic corrosion Increased corrosion in crevices or cracks or at contact surfaces between two metal articles.
 Selective corrosion Corrosive attack on structural constituents	 Exfoliation corrosion Occurs in deformed articles. Corrosion follows "fiber orientation".	 Interfacial corrosion Frequently observed at water-air interfaces⁽⁸⁾.

Figure : 1.2 The various types of corrosion are listed in the above table.

1.4 Factors Affecting Corrosion:

Corrosion is always the result of a combination of factors: physical, chemical, and biological. Physical factors include flow and temperature. Low-flow, dead-end areas typically have higher rates of corrosion. Erosion may cause corrosion in areas where water moves at extremely high velocities and at elbows. Corrosion tends to increase with higher temperatures—warmer summer months can result in higher corrosion rates, especially in surface water supplies. Chemical factors include alkalinity, hardness, conductivity, dissolved oxygen, and the presence of sulfates or chlorides. Low alkalinity limits the formation of a calcium carbonate coating and provides little resistance to pH change. Low hardness offers little protection in the form of calcium carbonate. Conductivity means the ability to transmit electricity. Some waters are more conductive than others. Because corrosion is an electrochemical process, the more conductive the water, the greater the potential for corrosion. Dissolved oxygen at levels greater than 3 to 5 mg/L can encourage corrosion. High levels of sulfates and chlorides can increase the rate of corrosion. Chlorides are a common problem where there is saltwater intrusion. Chlorides form soluble corrosion by-products that can cause pitting problems. Concerning biological factors, iron bacteria and sulfatereducing bacteria can speed both corrosion and the formation of corrosion by-products. Slime growths in the system or a musty or stale taste to the water give notice of these problems⁽⁵⁾.

1.4.1 Aqueous environment:

1.4.1.1 Influence of oxygen:

In air saturated water, the initial concentration rate at the room temperature reaches high and this rate diminishes over a period of days as rust film is formed and acts as a barrier to oxygen diffusion⁽³⁾.

1.4.1.2 Influence of velocity:

The velocity is affected by the factors like presence of oxygen, depends on characteristics of metal and environment to which is exposed. If the agitation increases, corrosion rate is also increases when oxygen presents in small amounts. In the distilled water, the critical concentration of oxygen above which corrosion decreases. This value increases with dissolved salts and with temperature, and decreases with increase in velocity pH⁽³⁾.

1.4.1.3 Influence of temperature

Temperature increases the rate of almost all chemical reactions. In an open vessel, allowing dissolved oxygen to escape, the rate increases with temperature to about 80°C and then falls to a very low value at the boiling point. The falling of the corrosion is indicated that decrease of oxygen solubility in water as the temperature raised. In a closed system, oxygen cannot escape and the corrosion rate continues to increase with temperature until all oxygen is consumed⁽³⁾.

1.4.1.4 Influence of pH

In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values⁽³⁾.

1.4.1.5 Influence of galvanic coupling

The general relation between penetration p (proportional to corrosion rate) of a metal having area A_a coupled to a more noble of area A_c , where p_o is the normal penetration of the metal uncoupled, is given by

$$P = p_o (1 + A_c/A_a) \quad (3)$$

If the ratio of areas A_c/A_a is large, the increased corrosion caused by coupling can be considerable⁽³⁾.

1.4.1.6 Influence of dissolved salts:

The corrosion rate first increases with salt concentration, then decreases, the value falling below that for distilled water when saturation is reached. Various salts like sodium chloride, Alkali-metal salts, Alkaline-earth salts, Acid salts etc. can affect the corrosion rate⁽³⁾.

1.5. Corrosion control:

Corrosion control achieved by recognizing and understanding corrosion mechanisms, by using corrosion-resistant materials and designs, and by using protective systems, devices, and treatments⁽¹⁾.

1.6. Copper:

Copper is metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys⁽⁹⁾. Copper alloys are widely used in many fields, especially for marine applications, such as seawater valves. As a

comparatively noble metal, copper has good resistance to corrosion in most cases. However, it still will undergo corrosion in such forms as pitting, crevice and stress corrosion cracking, and its alloys are subject to selective leaching . Among these types of corrosion, crevice corrosion is of particular interest to copper since valves are connected to piping systems with flanges and they contain numerous internal crevices⁽¹⁰⁾. Copper is characterised by good corrosion resistance. Nevertheless, staying for a long time in corrosive medium, it suffered the process of significant degradation, which was of electrochemical nature, of both local and general range⁽¹¹⁾.

1.6.1 Copper corrosion:

Even as a copper artefact leaves the foundry, its surface has already started to corrode. Corrosion is due to the interaction between a metal and its environment. This includes various electrochemical reactions, initially leading to an oxide layer on a metallic core. Copper oxides, carbonates and chlorides are the most commonly found compounds on the surface of archaeological copper and copper alloy artefacts. The products resulting from these deterioration processes are similar in composition to minerals found in nature. To a degree, these minerals are usually stable with respect to their environment. Excavated copper artefacts are usually covered by corrosion. The stability of the corrosion products depends on the burial environment of the object. Stable patina (noble patina) are normally found to be resistant to fluctuations in relative humidity⁽¹²⁾. One of the most important methods in the corrosion protection of copper is the use of organic inhibitors. Nitrogen and sulphur-containing organic heterocyclic compounds may act as inhibitors for copper dissolution due to the chelating action of heterocyclic molecules and the formation of a physical blocking barrier on the copper surface⁽¹³⁾.

1.6.2 Corrosion Forms Found in Copper and Its Alloys:

Copper and its alloys are subject to almost all kinds of corrosion attacks depending upon the environment. The following section is a summary of the relevant information from ASM handbook, on the types occurring on copper and its alloys⁽¹⁰⁾.

1.6.2.1 Uniform corrosion:

as far as copper and its alloys being concerned, the corrosion rate of copper is a little faster in oxidizing acid, sulfur-bearing compounds, NH_3 and cyanides .

1.6.2.2 Pitting:

Pitting of copper and its alloys always occurs under relatively low flow velocity. Long-term exposure tests have shown that there is a certain limit in pitting depth, beyond which an increase in pit depth is not obvious. To prevent a copper alloy from pitting, the correct choice of copper alloy for the environment is necessary. For example, aluminum brass is the best choice for protection against pitting attack, while the high-copper alloys are somewhat more inclined to pitting.

1.6.2.3 Erosion corrosion:

Copper alloys are relatively sensitive to erosion corrosion when they are exposed to water with high flowing velocity, and especially when turbulence occurs. Because rapidly flowing water can locally strip away any protective film, copper corrosion rates will be high.

1.6.2.4 Selective corrosion:

The dezincification of brass is the selective dissolution of the zinc from the alloy leaving a porous mass of copper with poor strength.

1.6.2.5 Stress corrosion cracking:

Stress corrosion cracking in copper materials is caused by tensile stresses, usually residual stresses from cold working, in combination with a corrosive which contains ammonia, moisture or mercury. In general, zinc-rich brass is most susceptible to stress corrosion cracking. However, under some conditions, other copper materials, even pure copper, can also be damaged by this type of corrosion.

1.6.2.6 Galvanic corrosion:

Copper and its alloys almost always serve as cathode due to their positions in galvanic series.

1.6.2.7 Crevice corrosion:

Classic crevice corrosion results from oxygen depletion and it attacks the inside crevice. For copper and its alloys, the reverse is true; the attack occurs on the surface outside the crevice while the crevice remains relatively corrosion-free.⁽¹⁰⁾

1.8 Corrosion inhibitor:

Definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of an inhibitor can be expressed by a measure of this improvement⁽¹⁾. Corrosion inhibitors are used

to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection, required⁽¹⁴⁾. Corrosion inhibitors industrial use find the widest application in recirculating systems. All of the organic inhibitors reviewed in this text are possibly toxic a description of health and safety measures taken during the experimental work can be found in appendix 8. Many inhibitors are effective for more than one type of metal, but ranges for pH, temperature and other conditions are often more specific. Some inhibitors suppress the anodic reaction, other inhibitors suppress the cathodic reaction. Some even suppress both electrochemical reactions. Inhibitor compounds are adsorbed to the surface of the corroded metal. An effective inhibitor has to be chemisorbed, by the means of electrostatic or van der Waals forces reacting rapidly with the electrode. The inhibitor is generally the electron donor and the metal the electron acceptor⁽¹²⁾. Inhibition of corrosion phenomena is an important subject of intense investigation due to the large economic losses it causes worldwide. The use of organic inhibitors is one of the most practical approaches for the corrosion protection of copper⁽¹⁴⁾.

1.7 Inhibition mechanism:

It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves the replacement of one or more water molecules adsorbed at the metal surface. The mixed-inhibition mechanism suggested by chemical and electrochemical investigations are consistent with Oguzie et al., and those of El Azhar et al. on the adsorption behavior of organic molecules containing both N and S atoms. In acid solutions, organic inhibitors may interact with the corroding metal and hence affect the corrosion reaction in more than one way, sometimes simultaneously. It is therefore often difficult to assign a single general inhibition mechanism, since the mechanism may change with experimental conditions. The presence of more than one functional group has been reported to often lead to changes in the electron density of a molecule, which could influence its adsorption behavior⁽¹³⁾.

1.9 Classification of Inhibitors:

Inhibitors have been classified differently by various authors. Some authors prefer to group inhibitors by their chemical functionality, as follows:

1.9.1 Inorganic inhibitors:

Usually crystalline salts such as sodium chromate, phosphate, or molybdate. Only the negative anions of these compounds are involved in reducing metal corrosion. When zinc is used

instead of sodium, the zinc cation can add some beneficial effect. These zinc-added compounds are called mixed-charge inhibitors.

1.9.2 Organic anionic:

Sodium sulfonates, phosphonates, or mercaptobenzotriazole (MBT) are used commonly in cooling waters and antifreeze solutions.

1.9.3 Organic cationic:

In their concentrated forms, these are either liquids or waxlike solids. Their active portions are generally large aliphatic or aromatic compounds with positively charged amine groups⁽¹⁾.

Inhibitor selection is based on the metal and the environment. A qualitative classification of inhibitors is presented in. Inhibitors can be classified into environmental conditioners and interface inhibitors⁽¹⁵⁾.

1.9.4 Environmental Conditioners (Scavengers):

Corrosion can be controlled by removing the corrosive species in the medium. Inhibitors that decrease corrosivity of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers. In near-neutral and alkaline solutions, oxygen reduction is a common cathodic reaction. In such situations, corrosion can be controlled by decreasing the oxygen content using scavengers.

1.9.5 Interface Inhibitors:

Interface inhibitors control corrosion by forming a film at the metal/environment interface. Interface inhibitors can be classified into liquid- and vapor-phase inhibitors.

1.9.6 Liquid-Phase Inhibitors:

Liquid-phase inhibitors are classified as anodic, cathodic, or mixed inhibitors, depending on sparingly soluble corrosion products, such as oxides, hydroxides, or salts, are formed. They whether they inhibit the anodic, cathodic, or both electrochemical reactions.

1.9.7 Anodic inhibitors:

Anodic inhibitors are usually used in near-neutral solutions where form, or facilitate the formation of, passivating films that inhibit the anodic metal dissolution reaction. Anodic inhibitors are often called passivating inhibitors. When the concentration of an anodic inhibitor is not sufficient, corrosion may be accelerated, rather than inhibited. The critical

concentration above which inhibitors are effective depends on the nature and concentration of the aggressive ions.

1.9.8 Cathodic inhibitors:

Cathodic inhibitors control corrosion by either decreasing the reduction rate (cathodic poisons) or by precipitating selectively on the cathodic areas (cathodic precipitators). Cathodic poisons, such as sulfides and selenides, are adsorbed on the metal surface; whereas compounds of arsenic, bismuth, and antimony are reduced at the cathode and form a metallic layer. In near-neutral and alkaline solutions, inorganic anions, such as phosphates, silicates, and borates, form protective films that decrease the cathodic reaction rate by limiting the diffusion of oxygen to the metal surface. Cathodic poisons can cause hydrogen blisters and hydrogen embrittlement due to the absorption of hydrogen into steel. This problem may occur in acid solutions, where the reduction reaction is hydrogen evolution, and when the inhibitor poisons, or minimizes, the recombination of hydrogen atoms to gaseous hydrogen molecules. In this situation, the hydrogen, instead of leaving the surface as hydrogen gas,

1.9.9 Mixed inhibitors:

About 80% of inhibitors are organic compounds that cannot be designated specifically as anodic or cathodic and are known as mixed inhibitors. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. Adsorption depends on the structure of the inhibitor, on the surface charge of the metal, and on the type of electrolyte. Mixed inhibitors protect the metal in three possible ways: physical adsorption, chemisorptions and film formation. Physical (or electrostatic) adsorption is a result of electrostatic attraction between the inhibitor and the metal surface. When the metal surface is positively charged, adsorption of negatively charged (anionic) inhibitors is facilitated. Positively charged molecules acting in combination with a negatively charged intermediate can inhibit a positively charged metal. Anions, such as halide ions, in solution adsorb on the positively charged metal surface, and organic cations subsequently adsorb on the. Physically adsorbed inhibitors interact rapidly, but they are also easily removed from the surface. Increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. The most effective inhibitors are those that chemically adsorb (chemisorb), a process that involves charge sharing or charge transfer between the inhibitor molecules and the metal surface .

1.9.10 Vapor-Phase Inhibitors:

Temporary protection against atmospheric corrosion, particularly in closed environments can be achieved using vapor-phase inhibitors (VPI). Substances having low but significant pressure of vapor with inhibiting properties are effective. The VPIs are used by impregnating wrapping paper or by placing them loosely inside a closed container. The slow vaporization of the inhibitor protects against air and moisture. In general, VPIs are more effective for ferrous than non-ferrous metals⁽¹⁵⁾.

Objectives of the study:

The objectives of this study can be summarize as follow:

- Study the corrosion of copper and copper alloy in different concentration of HNO_3 , H_2SO_4 , HCl , NaCl solutions.
- Evaluation and calculations of this corrosion.
- The inhibitions, kinetics and half life time of the copper and copper alloy corrosion.

Chapter two

Materials and Methods

2. Materials AND Methods

2.1 Materials:

2.1.1 Chemicals:

The following chemicals which includes nitric acid (HNO_3), hydrochloric acid (HCl), sodium chloride (NaCl), sulfuric acid (H_2SO_4), distilled water and acetone. were used in this research.

2.1.2 Apparatus:

250,400 ml beakers, sensitive balance, burette, copper ring, petri dish, volumetric flask 250ml.

2.1. 3 Methods:

2.1.3.1 Experimental works:

Similar sizes of copper and copper alloy $2 \times 2 \text{ cm}^2$ were exposed to different corrosive solution of HCl , NaCl , HNO_3 , and H_2SO_4 of different concentrations for seven days. The specimens were removed from the test solutions, and first washed with tap water. This was followed by washing in distilled water, cleaning with fine cloth, washing again with distilled water, and further washing with acetone. The specimens were finally weighed on an analytical balance, and the differences in weights before and after immersion of copper and copper alloy in the previous solutions at each interval were noted.

2.1.3.2. Specimens preparation:

Pure copper and copper alloy (bronze 90% copper and 10% Tin) was purchased from local market. Pieces of $2 \times 2 \text{ cm}^2$ square were cut copper and copper alloy, then degreased them by acetone, rinsed with distilled water dried and immersed in test solutions for specified period.

2.1.3.3. Measurement of Weight Loss :

The weight loss for one week was obtained using the weighing balance in different solutions of HCl , NaCl , HNO_3 , and H_2SO_4 and calculated the difference between the weight loss before and after one week of the immersion of the sample in the different solutions.

2.1.3.4. Determination of Corrosion Rate :

The most common method for estimating a corrosion rate from mass loss is to weight the corroding sample before and after exposure and divide by the total exposed area and the total

exposure time, making sure that appropriate conversion constants are used to get the rate in the required units. The method in mm/year can be represented by the following equation:

$$W.L = (W_b - W_a) \quad (2-1)$$

Where:

W_b and W_a are the weights before and after immersion in g.

2.1.3.5. Determination kinetic of corrosion and half life time:

Kinetic of corrosion and half life time can be calculated from the following equation:

$$K = 2.303/t * \log(\text{initial weight/mass loss}) \quad (2-2)$$

K =kinetic of corrosion

$$t_{1/2} = 0.693/K$$

$t_{1/2}$ =half life time

2.1. 3.6. Determination of Inhibitor efficiency :

Weight loss measurements were performed at room temperature by immersing copper and copper alloy test samples in 250 mL 1M (HNO_3 , H_2SO_4 , HCl , NaCl) solution in absence and presence of different concentrations of inhibitors urea and acetanilide (1.5 , 1 , 0.5 and 0.3 ppm by weight). The exposure time was optimized and optimized time (three days) was uniformly used for weight loss method. After three days exposure, test samples were cleaned. With distilled water and dried in a vacuum oven. The experiments were conducted for each weights of the inhibitors. The average of weight losses were taken, and inhibitor efficiency was calculated by the following equation

$$IE\% = (w_0 - w/w_0) \times 100 \quad (2-3)$$

Where:

W_0 is the corrosion rate in the absence of inhibitor, and w is the corrosion rate in the same Environment with the inhibitor added

$$R = (87.6 * W / D * A * T) \quad (2-4)$$

Where W = weight loss (mg).

R = Rate Inhibitor efficiency (MPY)

D = Density of sample (g/cm^3).

A = Area of specimen exposed to corrosion (cm^2).

T = Period of exposure (hrs)

Chapter three

Results and Discussion

CHAPTER THREE

3. Results and Discussion

3.1. Weight loss of the corrosion of pure copper /yr :

The test specimens were weighed before and after the exposure to the corrosion medium⁽¹⁶⁾ From table 3.1 and figure 3.2 it's clear that the weight loss increases with increasing concentration of HNO₃ and H₂SO₄. From the results obtained one could say that the amount of corrosion was found to be greater in HNO₃ than H₂SO₄ due to the strength of HNO₃ acid against H₂SO₄ acid. The reaction between copper and nitric acid (HNO₃) and sulfuric acid (H₂SO₄) can be represented by the following equations :

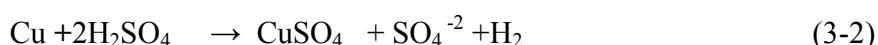
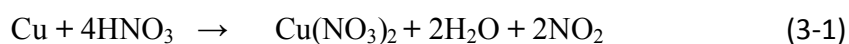


Table 3-1: Weight loss of the corrosion of pure copper in HNO₃ and H₂SO₄ were calculated from weight loss measurements at room temperature.

Concentration of HNO ₃ and H ₂ SO ₄	Weight loss /yr of HNO ₃	Weight loss /yr of H ₂ SO ₄
1	319	311.75
0.8	275.5	264.625
0.6	188.5	145
0.4	130.5	123.25

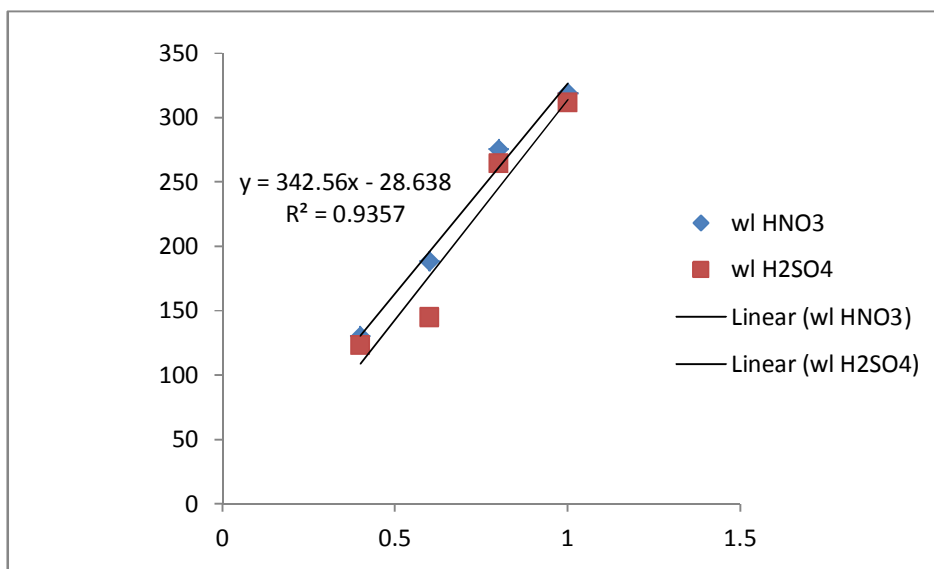


Figure 3-2 : relationship between weight loss/yr of pure copper and concentration of HNO_3 and H_2SO_4 .

Table 3.2 and figure 3.3 Showed that the weight loss increased with increasing concentration of HCl and NaCl. The reaction between copper and hydrochloric acid (HCl) and sodium chloride (NaCl), were shown in the below equations :

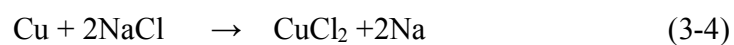
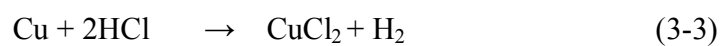


Table 3-2: Weight loss of the corrosion of pure copper in HCl and NaCl were calculated from weight loss measurements at room temperature.

Concentration of HCl and NaCl	Weight loss /yr of HCl	Weight loss /yr of NaCl
1	87	76.12
0.8	54.375	47.125
0.6	36.25	29
0.4	14.5	10.875

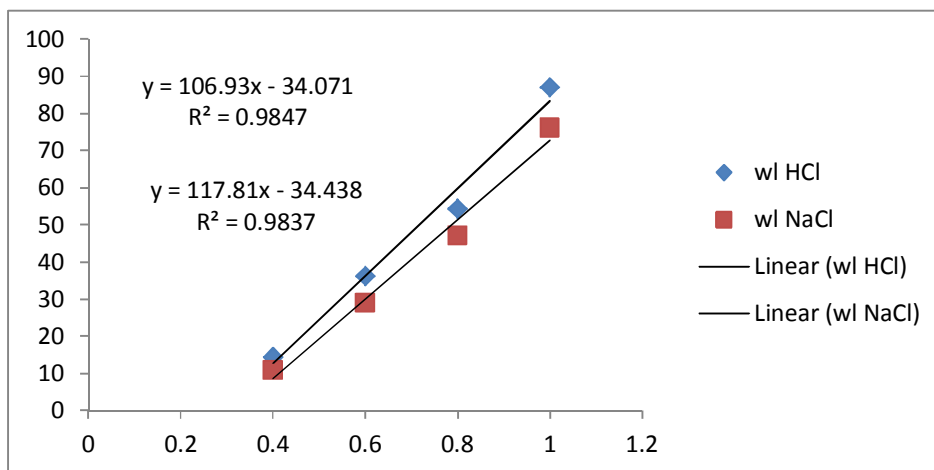


Figure 3-3 : relationship between weight loss/yr of pure copper and concentration of HCl and NaCl

3.2. Weight loss of the corrosion of copper alloy /yr :

Table.3.3 and curve .3.4the corrosion of copper alloy increased as the concentration of HNO_3 and H_2SO_4 increases this results were showed in table 3.3 and figure3.4 and in compersion between the corrosion of copper alloy and pure copper .which discussed in the previous result the corrosion of copper alloy low than pure copper due to the composition of copper alloy . which in addition to copper it composed tin which is more corrosion resistance than copper.

Table 3-3: Weight loss of the corrosion of copper alloy in HNO_3 and H_2SO_4 were calculated from weight loss measurements at room temperature.

Concentration of HNO_3 and H_2SO_4	Weight loss /yr of HNO_3	Weight loss /yr of H_2SO_4
1	235.625	217.5
0.8	184.875	155.875
0.6	141.375	83.375
0.4	61.625	43.50

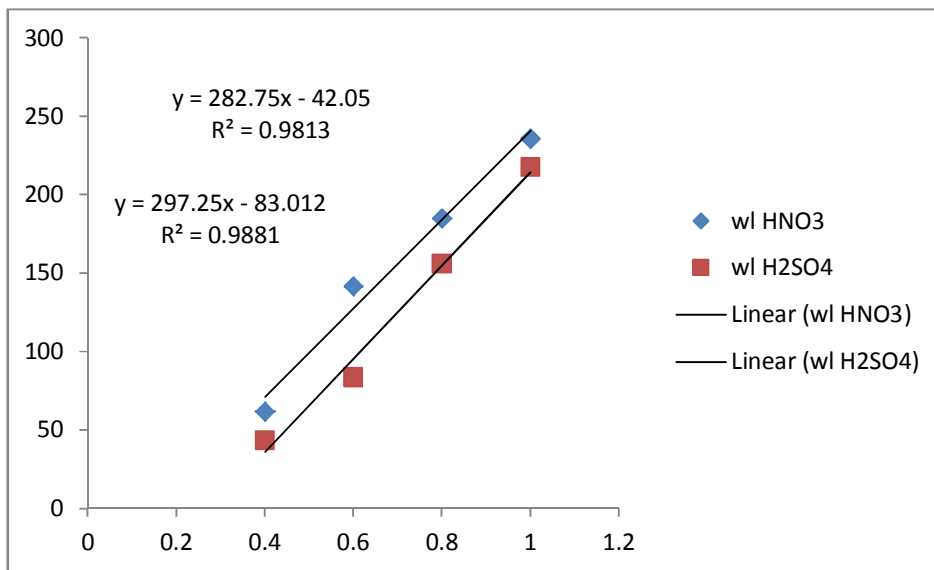


Figure 3-4 : relationship between weight loss/yr of copper alloy and concentration of HNO_3 and H_2SO_4 .

From table.3.4 and curve .3.5 its clear that the Weight loss per unit area and unit time of copper alloy increased with increasing concentration of HCl and NaCl .

Table 3-4: Weight loss of the corrosion of copper alloy in HCl and NaCl were calculated from weight loss measurements at room temperature.

Concentration of HCl and NaCl	Weight loss /yr of HCl	Weight loss /yr of NaCl
1	68.875	65.25
0.8	50.75	43.50
0.6	21.75	25.375
0.4	10.875	7.25

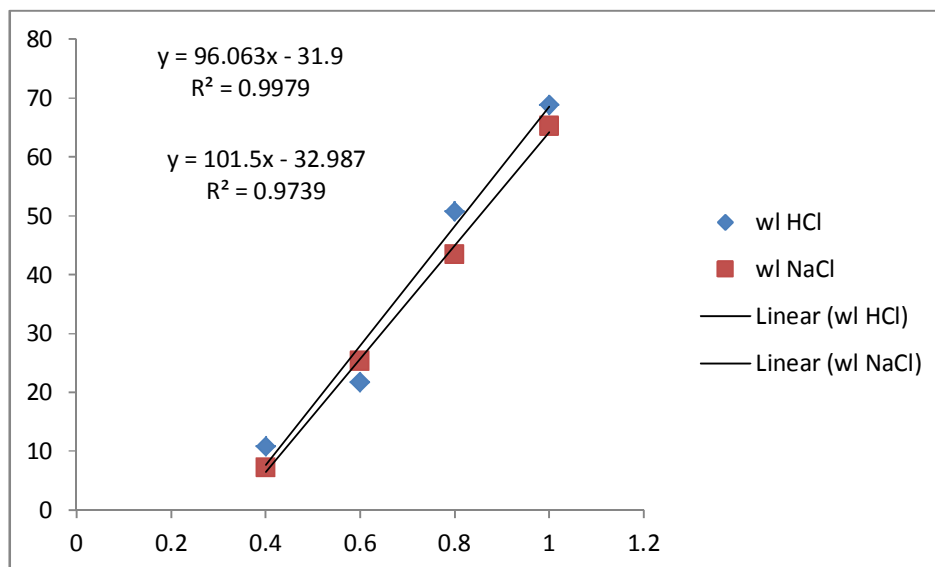


Figure 3-5: relationship between weight loss/yr of copper alloy and concentration of HCl and NaCl .

3.3. Kinetics of corrosion:

Corrosion, the environmental degradation of materials, is a complex process that depends on details of the environment and material, and is controlled by underlying thermodynamic and kinetic factors. The ultimate goal of a corrosion engineer is to predict and control the rate of corrosion. in the following paragraph the kinetic of corrosion of copper and copper alloy will be discussed.

3.3.1.pure Copper in different solution:

From table 3.5, copper sample was exposed to liquid environments, which include changing the content of the test media every seven days before and after re-immersing ,show in this tables the kinetics of corrosion increased with decreasing concentration of HNO_3 solution. and the half life time increased with increasing concentration of HNO_3 solution .

Table 3-5: Kinetics of corrosion and half life time of pure copper in HNO_3 :

NO of experiment	Concentration of HNO_3 (M)	K Specific reaction rate (min-1)	$t_{1/2}$ (min-1)
1	0.4	4.4108×10^{-09}	1.57×10^8
2	0.6	3.07330×10^{-09}	2.25×10^8
3	0.8	2.1309×10^{-09}	3.25×10^8
4	1	1.826×10^{-09}	3.79×10^8

From table3.6 and table 3.7 the kinetic of corrosion and half life time of pure copper in H_2SO_4 and HCl followed the same manner which discussed previously in HNO_3 solutions as indicate from table 3.6 and 3.7 and any variation in the value or degree of kinetic can be explained by the strength of corroded solution eg. HNO_3 greater than H_2SO_4 which in turn is greater than HCl

Table 3-6: Kinetics of corrosion and half life time of pure copper in H_2SO_4 :

NO of experiment	Concentration of H_2SO_4 (M)	K Specific reaction rate (min-1)	$t_{1/2}$ (min-1)
1	0.4	6.46566×10^{-09}	1.488×10^8
2	0.6	3.962×10^{-09}	1.78×10^8
3	0.8	2.1802×10^{-09}	2.47×10^8
4	1	1.86022×10^{-09}	3.725×10^8

Table 3-7: Kinetics of corrosion and half time of pure copper in HCl:

NO of experiment	Concentration of HCl (M)	K Specific reaction rate (min-1)	$t_{1/2}$ (min-1)
1	0.4	3.98×10^{-08}	7.41×10^6
2	0.6	1.61×10^{-08}	4.299×10^7
3	0.8	1.087×10^{-08}	6.37×10^7
4	1	6.695×10^{-09}	1.034×10^8

From table 3.8 the NaCl solution was chosen in this study because it's the major constituted of the sea water , the kinetic of corrosion and half life time of pure copper in NaCl was illustrated in the table 3.8

Table 3-8: Kinetics of corrosion and half life time of pure copper in NaCl :

NO of experiment	Concentration of NaCl (M)	K Specific reaction rate (min-1)	$t_{1/2}$ (min-1)
1	0.4	7.67×10^{-09}	9.030×10^7
2	0.6	1.201×10^{-08}	5.77×10^7
3	0.8	2.003×10^{-08}	3.459×10^7
4	1	5.2117×10^{-8}	1.32×10^7

3.3.2. Copper alloys in different solutions:

From tables 3.9 , 3.10, 3.11 and 3.12 the kinetic of corrosion and half life time of copper alloy in different aqueous medium which includes HNO_3 , H_2SO_4 , HCl and NaCl were shown in tables 3.9 to 3.12 respectively. One could say that the kinetic increased with decreasing acid concentration and the half life time increased with increasing acid concentration.

Table 3.9: Kinetics of corrosion and half life time of copper alloy in HNO₃ :

NO of experiment	Concentration of HNO ₃ (M)	K Specific reaction rate (min ⁻¹)	t _{1/2} (min ⁻¹)
1	0.4	1.519x10 ⁻⁰⁸	4.56x10 ⁷
2	0.6	6.61x10 ⁻⁰⁹	1.04x10 ⁸
3	0.8	5.12x10 ⁻⁰⁹	1.35x10 ⁸
4	1	4.02x10 ⁻⁰⁹	1.72x10 ⁸

Table 3-10: Kinetics of corrosion and half life time of copper alloy in H₂SO₄ :

NO of experiment	Concentration of H ₂ SO ₄ (M)	K Specific reaction rate (min ⁻¹)	t _{1/2} (min ⁻¹)
1	0.4	2.149x10 ⁻⁰⁸	3.22x10 ⁷
2	0.6	1.133x10 ⁻⁰⁸	6.11x10 ⁷
3	0.8	6.06x10 ⁻⁰⁹	1.142x10 ⁸
4	1	4.38x10 ⁻⁰⁹	1.58x10 ⁸

Table 3-11: Kinetics of corrosion and half life time of copper alloy in HCl :

NO of experiment	Concentration of HCl (M)	K Specific reaction rate (min ⁻¹)	t _{1/2} (min ⁻¹)
1	0.4	8.50x10 ⁻⁰⁸	8.15x10 ⁶
2	0.6	4.25x10 ⁻⁰⁸	1.62x10 ⁷
3	0.8	1.84x10 ⁻⁰⁸	3.76x10 ⁷
4	1	1.336x10 ⁻⁰⁸	5.187x10 ⁷

Table3-12: Kinetics of corrosion and half life time of copper alloy in NaCl :

NO of experiment	Concentration of NaCl (m)	K Specific reaction rate (min-1)	$t_{1/2}$ (min-1)
1	0.4	1.27×10^{-07}	5.426×10^6
2	0.6	3.68×10^{-08}	1.88×10^7
3	0.8	2.13×10^{-08}	3.25×10^7
4	1	1.42×10^{-08}	4.86×10^7

3.4. Inhibitor Efficiency:

Weight loss measurements were carried out in a 1.0 M (HNO₃, H₂SO₄, HCl, NaCl) in the absence and presence of different weights of urea and acetanilide. Corrosion rates of copper and copper alloy sample and the inhibition efficiency (IE%) were calculated using equation(2-3) . The results show that all urea and acetanilide used inhibit the corrosion of copper in 1.0 M (HNO₃, H₂SO₄, HCl, NaCl) solutions. The corrosion rate was found to depend on the weight of the urea and acetanilide. Increasing the weight of urea and acetanilide increases the inhibition efficiency IE% which reached its maximum value at weight. of 1.5g . This indicates that the protective effect of urea and acetanilide is not solely due to their reactivity with the nitric acid. The inhibitory behavior of urea and acetanilide against copper corrosion can be attributed to the adsorption of urea and acetanilide on the copper surface, which limits the dissolution of the latter by blocking of its corrosion sites and hence decreasing the corrosion rate, with increasing efficiency as their weight increase. These compounds can be adsorbed by the interaction between the lone pairs of electrons of the nitrogen, sulphur and oxygen atoms with the copper surface. This processes facilitated by the presence of d vacant orbitals of low energy in the copper ions, as observed in transition group metals. Recently it was found that the formation of donor–acceptor surface complexes between free electrons of an inhibitor and a vacant d orbital of a metal is responsible for the inhibition of the corrosion process. The active ingredients of organic inhibitors invariably contain one or more functional groups and containing one or more hetero atoms, N, O, S, P, or

Se (selenium), through .These groups are attached to a parent chain (backbone), which increases the ability of the inhibitor molecule to cover a large surface area⁽¹⁵⁾ .

3.4.1. Inhibitor Efficiency used urea in copper pure:

From tables 3.13 to 3.20 respectively. The inhibition efficiency values of the inhibitors (urea) at various weights at 25°C calculated by weight loss method have been given. It is evident from the data in the tables that inhibition efficiencies (IE%) of the inhibitors increased with increasing in weight of urea. the effectiveness of the inhibitor can be correlated with the structure and size of inhibitor molecule. Most of the organic compounds and metal complexes used as inhibitors have been found to inhibit corrosion process following the mechanism of adsorption. IE% of the inhibitor can be explained in term of the number of active centres for the adsorption, delocalized electron density and the projected surface area covered as a result of their adsorption. The inhibitors(urea) consist of two nitrogen atoms and functional group as active centres and delocalized π -electron density urea causing a high % IE% for the inhibitor⁽¹⁷⁾ . The corrosion rate of inhibitor (R) of the pure copper and copper alloy were estimated as observed from the experiments .

Table3-13: Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of pure copper after three days immersion in 1M HNO₃ at 25°C.

Weight of Urea (g)	Weight loss of HNO ₃ (g)	Efficiency (IE%)	R (MPY)
1.5	0.466	52.9	6.37×10^2
1	0.418	47.5	5.71×10^2
0.5	0.375	42.6	5.12×10^2
0.3	0.325	36.9	4.42×10^2

Table3-14: Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of pure copper after three days immersion in 1M H₂SO₄ at 25°C.

Weight of Urea (g)	Weight loss of H ₂ SO ₄ (g)	Efficiency (IE%)	R (MPY)
1.5	0.459	53.3	6.27X10 ²
1	0.415	48.2	5.67X10 ²
0.5	0.370	43	5.05X10 ²
0.3	0.320	37.2	4.37X10 ²

Table3-15 : Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of pure copper after three days immersion in 1M HCl at 25°C.

Weight of Urea (g)	Weight loss of HCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.152	63.3	2X10 ²
1	0.141	58.7	1.92X10 ²
0.5	0.120	50	1.64X10 ²
0.3	.091	37.9	1.24X10 ²

Table3-16: Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of pure copper after three days immersion in 1M NaCl at 25°C.

Weight of Urea (g)	Weight loss of NaCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.144	68.5	1.69×10^2
1	0.128	60.9	1.74×10^2
0.5	0.119	56.6	1.62×10^2
0.3	0.090	42.8	1.23×10^2

3.4.2. Inhibitor Efficiency used urea in copper alloy:

Table3-17 : Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of copper alloy after three days immersion in 1M HNO₃ at 25°C .

Weight of Urea (g)	Weight loss of HNO ₃ (g)	Efficiency (IE%)	R (MPY)
1.5	0.311	47.8	4.25×10^2
1	0.288	44.3	3.93×10^2
0.5	0.230	35.3	3.14×10^2
0.3	0.156	24	2.13×10^2

Table3-18 : Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of copper alloy after three days immersion in 1M H₂SO₄ at 25°C.

Weight of Urea (g)	Weight loss of H ₂ SO ₄ (g)	Efficiency (IE%)	R (MPY)
1.5	0.309	51.5	4.22×10^2
1	0.275	45.8	3.75×10^2
0.5	0.225	37.5	3.07×10^2
0.3	0.152	25.3	2.07×10^2

Table 3-19 : Inhibition efficiency (IE) and surface coverage at different weights of urea for the corrosion of copper alloy after three days immersion in 1M HCl at 25°C.

Weight of Urea (g)	Weight loss of HCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.12	63.1	1.64×10^2
1	0.1	52.6	1.36×10^2
0.5	0.090	47.3	1.23×10^2
0.3	0.081	42.6	1.10

Table 3-20 : Inhibition efficiency (IE%) and surface coverage at different weights of urea for the corrosion of copper alloy after three days immersion in 1M NaCl at 25°C.

Weight of Urea (g)	Weight loss of NaCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.119	66.1	1.62×10^2
1	0.096	53.3	1.31×10^2
0.5	0.085	47.2	1.16×10^2
0.3	0.079	34.2	1.07×10^2

The results were shown in the this Tables. The corrosion rates of inhibitor(R) of the pure copper and copper alloy it were generally observed in this tables that were decreased in weight with decreasing weight of inhibitor in This tables, because increased acidity or alkalinity is one of the conditions for increasing corrosion depending on other prevailing conditions in each environment ⁽¹⁸⁾, The inhibition efficiency increased with increasing in weight of the inhibitors(urea). Also the values of inhibition efficiency obtained at different weight of urea⁽¹⁹⁾. The inhibition efficiency was found maximum up 68.5 to be greater in NaCl for pure

copper by using inhibitor (urea), because the strength alkalinity of NaCl compared with other solutions in this research.

3.4.3. Inhibitor Efficiency used acetanilide in copper pure:

The inhibition efficiencies (IE%) at different weight of acetanilide for the corrosion of pure copper and copper alloy after three days in different aqueous medium its include HNO_3 , H_2SO_4 , HCl and NaCl were shown in tables 3.21 to 3.28 respectively .note that the inhibitor (acetanilide)contain functional groups and containing one hetero atom, (N) . These groups were increased the ability of the inhibitor molecule to cover a large surface area⁽¹⁵⁾. The corrosion rate of inhibitor (R) of the pure copper and copper alloy were estimated as observed from the experiments .

Table 3-21: Inhibition efficiency (IE%) and surface coverage at different weightsof acetanilide for the corrosion of pure copper after three days immersion in 1M HNO_3 at 25°C.

Weight of acetanilide(g)	Weight loss of HNO_3 (g)	Efficiency (IE%)	R (MPY)
1.5	0.455	51.7	6.22×10^2
1	0.394	44.7	5.38×10^2
0.5	0.321	36.4	4.38×10^2
0.3	0.242	27.5	3.30×10^2

Table3-22: Inhibition efficiency (IE%) and surface coverage at different weights of acetanilide for the corrosion of pure copper after three days immersion in 1M H_2SO_4 at 25°C.

Weight of acetanilide (g)	Weight loss of H_2SO_4 (g)	Efficiency (IE%)	R (MPY)
1.5	0.450	52.3	6.15×10^2
1	0.389	49.1	5.31×10^2
0.5	0.319	45.2	4.36×10^2
0.3	0.241	28	3.29×10^2

Table 3-23 : Inhibition efficiency (IE%) and surface coverage at different weights of 25°C acetanilide for the corrosion of pure copper after three days immersion in 1M HCl at 25°C.

Weight of acetanilide (g)	Weight loss of HCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.147	61.2	2.00×10^2
1	0.139	57.9	1.90×10^2
0.5	0.117	48.8	1.60×10^2
0.3	0.089	37	1.21×10^2

Table 3-24 : Inhibition efficiency (IE%) and surface coverage at different weights of acetanilide for the corrosion of pure copper after three days immersion in 1M NaCl at 25°C.

Weight of acetanilide (g)	Weight loss of NaCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.142	67.6	1.94×10^2
1	0.124	59	1.69×10^2
0.5	0.116	55.2	1.58×10^2
0.3	0.089	42.3	1.21×10^2

3.4.4. Inhibitor Efficiency used acetanilide in copper alloy:

Table 3-25 : Inhibition efficiency (IE%) and surface coverage at different weights of acetanilide for the corrosion of copper alloy after three days immersion in 1M HNO₃ at 25°C.

Weight of acetanilide (g)	Weight loss of HNO ₃ (g)	Efficiency (IE%)	R (MPY)
1.5	0.28	43	3.82×10^2
1	0.24	36.9	3.28×10^2
0.5	0.21	32.3	2.87×10^2
0.3	0.15	23	2.05×10^1

Table 3-26 : Inhibition efficiency (IE%) and surface coverage at different weights of acetanilide for the corrosion of copper alloy after three days immersion in 1M H₂SO₄ at 25°C.

Weight of acetanilide (g)	Weight loss of H ₂ SO ₄ (g)	Efficiency (IE%)	R (MPY)
1.5	0.265	44.1	3.62×10^2
1	0.224	37.3	3.06×10^2
0.5	0.20	33.3	2.73×10^2
0.3	0.144	24	1.96×10^2

Table 3-27: Inhibition efficiency (IE%) and surface coverage at different weights of acetanilide for the corrosion of copper alloy after three days immersion in 1M HCl at 25°C.

Weight of acetanilide (g)	Weight loss of HCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.112	58.9	1.53×10^{-2}
1	0.091	47.8	1.24×10^{-2}
0.5	0.085	44.7	1.16×10^{-2}
0.3	0.075	39.4	1.01×10^{-2}

Table 3-28: Inhibition efficiency (IE%) and surface coverage at different weights of acetanilide for the corrosion of copper after three days immersion in 1M NaCl at 25°C.

Weight of acetanilide (g)	Weight loss of NaCl(g)	Efficiency (IE%)	R (MPY)
1.5	0.111	61.6	1.51×10^{-2}
1	0.090	50	1.23×10^{-2}
0.5	0.083	46.1	1.13×10^{-2}
0.3	0.074	41.1	1.01×10^{-2}

The results were shown in the tables the inhibition efficiency (IE%) by using inhibitor (acetanilide) of pure copper and copper alloy increased with increasing in weight of the inhibitors (acetanilide). Corrosion rate (R) slow-down in tables because a film of Cu^{1+} oxide retards the diffusion between the solution and copper surface. The inhibition efficiency was found maximum up 67.6 to be greater in NaCl for pure copper by using inhibitor (acetanilide), because the strength alkalinity of NaCl compared with other solutions in this research.

If we compare between urea and acetanilide in the above tables we Note that Urea was found to be a better inhibitor than acetanilide, due to containing two hetero atoms (N) but acetanilide containing one hetero atom (N) that was active ingredients of organic inhibitors. in the tables

shown that the values of inhibition efficiency obtained at different weight of urea and acetanilide⁽¹⁹⁾. Also note the results inhibition efficiency (IE%) of copper alloy low than pure copper due to composition of copper alloy its addition to pure copper it composed of tin which is more inhibition resistance than copper .

4. Conclusion:

- Corrosion is a complex series of reactions between different environmental conditions and metal surfaces.
- The studied pure copper and copper alloy corrodes in HNO_3 , H_2SO_4 , HCl , NaCl solutions with a first order reaction and the corrosion rate increased with the increasing in acid concentration .the kinetic of corrosion increase with decrease concentration .
- Corrosion rate slow-down in tables a film of Cu^{1+} oxide retards the diffusion between the solution and copper surface.
- The choice of the inhibitors was based on the fact that these compounds contains electrons and hetero atoms such as N, O and S, which involve greater adsorption of the inhibitor molecules onto the surface of copper.
- The order of effectiveness of the corrosion inhibitors evaluated was urea > acetanilide .
- Weight loss technique has been used to study the corrosion inhibition efficiency of in 1.0 M (HNO_3 , H_2SO_4 , HCl , NaCl) solutions by using the urea and acetanilide The results show that urea is good corrosion inhibitors.
- Corrosion inhibition efficiency increased with increasing weight of inhibitor. Inhibition efficiency was found maximum up to 66.6% for copper. and corrosion rate of inhibitor increase with increase concentration .

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