CORROSION INHIBITION OF MILD STEEL IN 1 M HCl SOLUTION BY *CURCUMA LONGA* RHIZOME EXTRACT

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by

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AC	alternating current
AR	analytical reagent
BDMC	Bisdemethoxycurcumin
CE	counter electrode
CR	corrosion rate
DC	direct current
DMC	demethoxycurcumin
EDX	energy analysis dispersive X-rays
EIS	electrochemical impedance spectroscopy
EW	equivalent weight
FTIR	fourier transform infrared spectroscopy
GAE	gallic acid equivalents
IE	inhibition efficiency
LCMS	liquid chromatography mass spectrometry
MS	mild steel
OCP	open circuit potential
PZC	potential of zero charge
RE	reference electrode
SCE	saturated calomel electrode
SEM	scanning electron microscopy
TPC	total phenolic content
UV-Vis	ultraviolet-visible
WE	working electrode

LIST OF SYMBOLS

C	capacitance
C_{dl}	double layer capacitance
CPE	constant phase element
E	electrode potential
E_{corr}	corrosion potential
E_{pzc}	potential of zero charge
ω	frequency
ΔG	Gibbs energy
i_{c}	current density
I	current
i_0	exchange current density
i_{a}	partial anodic current density
i_{c}	partial cathodic current density
i_{corr}	corrosion current density
i_{meas}	net measurable current density
a	real component
L	inductance
n	constant phase element exponent (phase shift)
η	cell overvoltage
$\eta\%$	percentage inhibition efficiency
R	molar gas constant
R_{ct}	charge transfer resistance
R_{p}	polarization resistance

R_s	solution resistance
T	absolute temperature
$\| Z \|$	absolute value of complex number
Y_0	constant phase element coefficient
Z	impedance of ac circuits
β	Tafel slope
β_a	anodic Tafel constant
β_c	cathodic Tafel constant
Φ	phase angle
ω	angular ac frequency
V	voltage signal
$q(t)$	electric charge
W	Warburg
L	inductor
Z'	real impedance
Z''	imaginary impedance
Z	impedance
λ_{max}	maximum wavelength absorption
f_{max}	maximum frequency
h	Plank’s constant
N	Avogadro’s number
t	time
ΔW	weight loss
A	total area
ΔH	enthalphy of activation

ΔS	entropy of activation
Θ	surface coverage
w_L	weight loss
R^2	linear correlation coefficient

PERENCATAN KAKISAN BAGI KELULI LEMBUT DALAM LARUTAN 1 M HCl OLEH EKSTRAK RIZOM *CURCUMA LONGA*

ABSTRAK

Tindakan perencatan oleh ekstrak *Curcuma longa* atau lebih dikenali sebagai kunyit untuk merencat kakisan keluli lembut dalam larutan 1 M HCl telah dikaji. Kesan sembilan jenis pelarut (berdasarkan tertib kekutuban) terhadap keterlarutan *Curcuma longa* telah diselidik. Kajian membuktikan bahawa *Curcuma longa* yang telah diekstrak menggunakan 95% larutan akueus ethanol memberikan keterlarutan dan jumlah ekstrak yang tertinggi. Kajian pencirian telah dijalankan untuk mengenalpasti kandungan curcumin yang merupakan kandungan aktif. Keputusan spektroskopi inframerah fourier (FTIR) mencadangkan kewujudan kumpulan fungsi utama yang memenuhi ciri keperluan sebagai perencat kakisan organik yang baik. Berdasarkan penyerapan maksima (λ_{max}) oleh ekstrak *Curcuma longa* dari spektroskopi UV-Visible (UV-Vis) membuktikan dengan kukuh akan kehadiran curcumin. Kajian curcuminoids dengan menggunakan jisim spektroskopi kromatografi cecair (LCMS) fasa terbalik dengan menggunakan kolum C18 menunjukkan curcumin, demethoxycurcumin (DMC) dan bisdemethoxycurcumin (BDMC) telah diasingkan. Kesan ekstrak *Curcuma longa* dan curcumin piawai sebagai rujukan bagi keluli lembut di dalam larutan berasid telah dijalankan. Ekstrak *Curcuma longa* memberikan 70% kecekapan perencatan kakisan pada kepekatan 80 ppm. Pengukuran kekutuban potentiodinamik mendedahkan perencat berkelakuan sebagai perencat jenis campuran, yakni merencat kedua-dua tindak balas anodik dan kathodik. Pengukuran spektroskopi elektrokimia impedan (EIS) mendapati proses pertukaran cas adalah faktor utama yang mengawal reaksi kakisan. Berdasarkan pengukuran keupayaan cas sifar (PZC), permukaan keluli bercas negatif dan bertanggungjawab untuk penjerapan elektrostatik oleh molekul berproton daripada ekstrak *Curcuma longa*. Keberkesanan perencatan oleh ekstrak bertambah dengan bertambahnya kepekatan, tetapi berkurang dengan bertambahnya suhu (30-55 ^{o}C). Pengaktifan, isoterma dan pengukuran termodinamik yang mengawal proses penjerapan telah dikira dan dibincangkan. Dengan bertambahnya kepekatan perencat, bertambahnya tenaga pengaktifan, tenaga pengaktifan entalpi dan tenaga pengaktifan entropi telah didapati. Keputusan menunjukkan yang perencatan adalah secara penjerapan fizikal dengan tindak balas endoterma dan proses penjerapan adalah lebih ke arah suhu rendah dengan tenaga bebas piawai yang lebih besar. Proses penjerapan adalah sesuai dipadankan dengan model penjerapan Langmuir dan El-Awady. Analisis permukaan elektron menunjukkan permukaan keluli yang mengandungi perencat adalah lebih sekata dan bebas daripada kakisan yang teruk.

CORROSION INHIBITION OF MILD STEEL IN 1 M HCl SOLUTION BY *CURCUMA LONGA* RHIZOME EXTRACT

ABSTRACT

The inhibitive action of the extract of *Curcuma longa* or generally known as turmeric for mild steel corrosion inhibitor in 1 M HCl solution was investigated. The effect of nine solvent systems (based on polarity) on the solubility of *Curcuma longa* has been studied. It was revealed that the *Curcuma longa* extracted with 95% aqueous ethanol gave the highest solubility and extraction yield. Characterization studies have been conducted to determine the curcumin content which is the active ingredient. Fourier transform infrared (FTIR) spectroscopy results suggest the presence of important functional groups that can fulfil the requirement as a potent organic corrosion inhibitor. The experimental findings based on the maximum absorption (λ_{max}) of the *Curcuma longa* extract from the UV-Visible (UV-Vis) spectroscopy gives strong evidence on the presence of curcumin. The analysis of curcuminoids by means of reversed phase liquid chromatography mass spectrometry (LCMS) using C18 column have shown that curcumin, demethoxycurcumin (DMC) and bisdemethoxycurcumin (BDMC) were separated. The effect of *Curcuma longa* extract and standard curcumin as reference were investigated as corrosion inhibitors for mild steel in acidic media. The *Curcuma longa* extract exhibited 70% corrosion inhibition efficiency at 80 ppm concentration. Potentiodynamic polarization measurement revealed that the inhibitors behave as mixed type inhibitor, promoting retardation of both anodic and cathodic reactions. The electrochemical impedance spectroscopy (EIS) revealed that the charge transfer was the main controlling factor of the corrosion reaction. From the potential of zero charge (PZC) measurement, the negatively charged metal surface might be responsible for the electrostatic adsorption of the protonated molecules. Inhibition efficiency of the extract increased with the increase in concentration but decreased with the increase in temperature (30-55 ^{o}C). The activation, isotherm and thermodynamic parameters governing the adsorption process were calculated and discussed. As the concentrations of the inhibitors increased, higher activation energy, enthalphy of activation and entropy of activation were obtained. Results revealed that the inhibition were physisorption in nature with an endothermic reaction and the adsorption process was more favoured at lower temperatures with larger negative standard free energy. The adsorption process was well fitted with the Langmuir and El-Awady adsorption isotherm. The scanning electron micrographs showed that the surface of mild steel in the inhibited solution were smooth and free from any serious corrosion.

CHAPTER 1

INTRODUCTION

1.1 Background, problem statement and significance of study

Corrosion destroys metals by converting them into oxides or other corrosion products. Corrosion is an inevitable phenomena and a natural occurring process where it can be defined as the deterioration of a material's properties due to its interaction with its surroundings. Corrosion can induce to failings in plant equipment and machines that are normally costly to repair, in terms of environmental damage, loss of contaminated products and possibly costly in terms of human health or life. Corrosion also affects the total world supply of metals by removing components or structures from service, thus, their replacement consumes a portion of the total supply of the earth's material resources. Materials reliability is becoming ever more critical in our society nowadays, particularly in terms of the liability issues that develop when reliability is not guaranteed, safety is compromised, and thus, failure occurs. Taking this into account, considerable attempts and efforts are generally being expended here and there in corrosion control at the design stage and in the operational phase, also in corrosion monitoring, especially for industries where harsh chemicals are handled regularly.

The driving force that causes metals to corrode is due to the natural consequence of their temporary existence in metallic form. The primary corrosion product of iron exists as, eg. $Fe(OH)_2$, or more likely $FeO{\bullet}nH_2O$, however the action of water and oxygen can yield other products having different colours (Roberge, 2008); (i) $Fe_2O_3{\bullet}H_2O$ or hydrous ferrous hydroxide, sometimes written as $Fe(OH)_3$, is the principle component of red-brown rust. It can form a mineral called hematite which is the most common iron ore, (ii) $Fe_3O_4 \bullet H_2O$ or hydrated magnetite, known as ferrous ferrite, written as ($Fe_2O_3 \bullet FeO$), most often green but can be deep blue in the presence of organic complexants, (iii) Fe_3O_4 or magnetite which is black.

Mild steel being the important alloy of iron has found a wide application in industries, constructional materials and machines due to its low cost and excellent mechanical properties despite of its tendency to corrosion in aqueous solution, especially in acidic media (Badr, 2009; Döner and Kardas, 2011; Pavithra et al., 2012; Tao et al., 2012). Acid solutions on the other hand are often used in the industry for industrial acid cleaning, pickling, descaling, oil well acidizing and petrochemical processes which are normally accompanied by considerable dissolution of metal (Amin et al., 2007; Bayol et al., 2008; Kardaş, 2005; Keleş, 2011; Oguzie, 2008).

A few methods are used to control the corrosion process, however the application of inhibitors has been proven to be the most promising, effective, flexible and cost attractive method for the purpose of slowing down the corrosion rate of metals. Corrosion inhibitors are chemical compound that are used in small concentration which when added to a corrosive media retards the corrosion process and keeps its rate to a minimum (El-Etre, 2007; Raja and Sethuraman, 2008). However, inorganic compounds like chromate and dichromate that are widely used in industrial applications are known to be toxic, expensive and non-environmental friendly, thus, these factors limit their applications (Amin et al., 2007). Many environmental legislations have been made to impose and to divert researchers to the use of environmental friendly natural products from renewable resources. As a result, research into relatively non-toxic, inexpensive, readily available and ‘green’ corrosion inhibitor by using inedible or edible plant extracts that come from leaves, rhizomes, seeds or bark have been reported as an alternative substitution. Plant extracts are known to provide rich sources of naturally synthesized chemical compounds that can be extracted by simple methods. Researchers have studied the corrosion inhibition activity of plant extracts on different types of metals in different environment due to the environmental point of view. It was successfully reported that they could effectively act as potential inhibitors for metals. For example, aqueous extracts of orange peels and mango, passion fruits and cashew peels (da Rocha et al., 2010), caffeic acid (de Souza and Spinelli, 2009), *Aleo vera* (Abiola and James, 2010), *Ginkgo* leaves (Deng and Li, 2012), extract of *Punica granatum* and their main constituents (Behpour et al., 2012) have been reported to be efficient corrosion inhibitors for steel in acidic solutions.

Studies revealed that heteroatoms such as nitrogen, oxygen, sulphur and phosphorus, compounds bearing π electrons in triple or conjugated double bonds possess the ability to act as good corrosion inhibitor as they are easily adsorbed onto the metal surface through physical and/or chemical adsorption, thus altering corrosion susceptibility (Gopiraman et al., 2012; Obot and Obi-Egbedi, 2010; Valek and Martinez, 2007; Wang et al., 2011; Yǖce and Kardaş, 2012). It is widely accepted that organic inhibitors exhibit corrosion via adsorption. The inhibition mechanism is a separation process involving the process where (i) the inhibitor is being adsorbed on the surface of the metal forming a compact protective thin layer and (ii) the inhibitor forms a precipitate on the surface of the metal, acting on the aggressive media to form protective precipitates or to remove the aggressive agents (El-Sayed et al., 2010).

Adsorption, on the other important notes can be described by two main types of interaction, which are physisorption and chemisorption (Levine, 1995), where; (i) *Physisorption*: involves electrostatic forces between ionic charges or dipoles on the adsorbed species and the electric charge at the metal/solution interface. Since the heat of adsorption is low, thus, this adsorption is only stable at relatively low temperature and (ii) *Chemisorption*: involves charge transfer or sharing of electrons from the inhibitor molecules to the metal surface to form a coordinate type bond. This type of adsorption is known to have much stronger adsorption energy compared to the other mode of adsorption. Thus, such bond is more stable at higher temperature.

Curcuma longa or commonly known as turmeric that comes from Zingiberaceae family are widely cultivated in the tropical regions of Asia, most extensively in Latin America and India. *Curcuma longa* is profoundly used in traditional Chinese medicine and Ayurveda for the past thousand years. *Curcuma longa* has also long been used as food colorant and spice in Southeast Asia. It is known that curcumin; 1,7-bis(4-Hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione is the major active compound found in *Curcuma longa* (Ravindran et al., 2010). The phenolic compounds, namely curcuminoids, constituted approximately 1-5% of *Curcuma longa* are responsible for the yellow colour characteristic of the root. These curcuminoids composed mainly of curcumin, demethoxycurcumin and bisdemethoxy curcumin are known to have high anti-oxidant activities due to the presence of hydroxyl group (Maizura et al., 2011).

Curcumin possesses diverse pharmacological effects, including anti-inflammatory, anti-oxidant, anti-proliferative activities, anti-microbial, anti-cancer etc. (Ghosh et al., 2011; Gilda et al., 2010). The antioxidant activities are related to the ability to donate H radical from phenolic hydrogen of the hydroxyl groups to the radical species. Therefore, the more the hydroxyl groups present in a given compound, the greater the antioxidant activities. Previous studies on the use of tannins having multiple phenolic groups that have very high affinities for iron have been reported as inhibitors of metals through adsorption on metal surfaces and by passive film formation at the metal surfaces forming ferric-tannate complex (Elhabiri et al., 2007; Iglesias et al., 2001). Several studies have also shown that antioxidant activities and phenolic content correlate very well together (Du et al., 2009; Silva et al., 2007; Turkmen et al., 2006).

By considering all the mentioned points stating the use of other polyphenolic compounds and the fact that *Curcuma longa* itself is a rich source of antioxidant and due to the presence of important functional groups in its structure, thus, it is the aim of this study to evaluate the potential use of *Curcuma longa* extract as corrosion inhibitor for mild steel in acidic media. This is due to the point that the chemical sturucture of curcumin itself, which is the main active compound in *Curcuma longa*, possess the central methylene hydrogen, hydroxyl, oxygen, heterocyclic compounds with polar functional group and conjugated double bond that show the ability to act as organic corrosion inhibitor. With multiple phenolic groups that have high affinities for iron, curcuminoids are believed to act as inhibitors by film forming on metal surfaces. However, despite all of the features stated, curcuminoids have low aqueous solubility (Tapal and Tiku, 2012). In order for a compound to act as corrosion inhibitor, they must be made soluble in aqueous solution. To the best of our knowledge, inhibition studies of curcumin have been done on carbon steel in basic solution or by blending the extracted compound with the most common cooling water inhibitor, HEDP or also known as biphosphonate (Farooqi et al., 1999; Kandias et al., 2009; Rajendran et al., 2005), but it is not known yet whether it works in an acidic environment for mild steel surfaces. Before the main study is being carried out for the application purposes, it is always easier to study the pure compound of the plant extracts first as little is known about the exact composition of the plant extracts. In addition, the pure synthetic compound is also important as a benchmark and reference for the plant extracts. This is because it is almost impossible to construct a simple extraction method like the one design in this study that yields totally pure curcumin in the extract.

1.2 Research objectives

The aim of this work is to evaluate the corrosion inhibition of *Curcuma longa* extract for mild steel in 1 M HCl solution. In order to achieve this aim, therefore, the objectives of the present work are divided into several points as follows:

i. To study the effects of solvent polarity on the solubility and phenolic content of *Curcuma longa* extract.

ii. To study the corrosion inhibitive effect of the *Curcuma longa* extract on mild steel in 1 M HCl solution.

iii. To determine the inhibition mechanism of the *Curcuma longa* extract through isotherm and thermodynamic studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion

Corrosion is more than just an inevitable natural phenomenon. It is very important from the points of view in economics and tragic accidents involving loss of life. Corrosion can be very expensive as well as unsafe to us as a human and surroundings. Corrosion chemistry itself is changing at a rapid phase and each chemical process is viewed critically and deeply from the points of view in safety, environmental impact and economics.

The term “corrosion” has its origin in Latin where the Latin word “*rodere*” means “gnawing” and “*corrodere*” means “gnawing to pieces”. However, to most of us, it is always easier to describe corrosion as rusting. Corrosion can be defined as deterioration of metals and its alloy due to chemical and electrochemical reaction with its surrounding. In everyday life, corrosion manifests itself in many terms, such as corroded automobiles, pipes, boilers, nails, pots, tanks, rail, petroleum and petrochemical operations. Everybody is certain that corrosion is an immense problem. The impact of corrosion is felt and affects many sectors of the national economy worldwide. The elements involving the costs of corrosion are concerned with design, control, and capital as well as associated costs. The high costs of corrosion have contributed a significant effect on the national economy, therefore it is necessary for each of the corrosion personnel to adapt the corrosion control measures in order to minimize corrosion losses.

Most metals occur in nature as compounds such as oxides and carbonates with very few metals occur in native form. The driving force that causes metal to corrode is a natural consequence of their temporary existence in metallic form or in other words; the obvious reason is the thermodynamic stability of compounds as opposed to the metals. Therefore, corrosion is an extractive metallurgy in reverse as shown in Figure 2.1. Extraction of a metal from ore is known as reduction process. In order to reach this metallic state from their occurrence in nature in the form of ores, it is necessary for the metals to release energy that is return to its original form through the corrosion process.

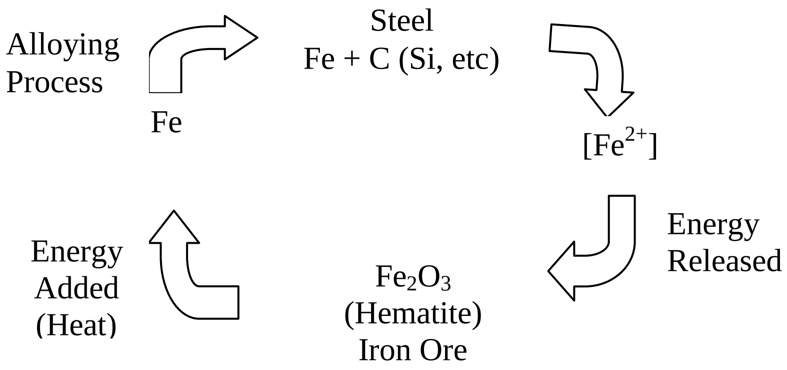

Figure 2.1 Corrosion cycle of iron.

The energy needed to convert iron ore to metallic iron is returned when the iron corrodes to form the original compound. The atmospheric corrosion of iron steel often results in the formation of iron oxyhydroxides such as goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and akagonite (β-FeOOH) as well as iron oxides such as magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). However, magnetite, goethite, and lepidocrocite are the stable oxides that are usually formed in all rusty steel surfaces under ambient conditions. The corrosion behaviour of the materials depends on the environment to which they are subjected and the corrosivity of the environment depends on the entire surroundings in contact with that material.

Corrosion cannot be defined without a reference to environment as all environments are corrosive to some degree. Most metals corrode when being in contact with water or moisture, acids, bases, salts, oils, natural, urban, marine and industrial atmospheres, aggressive metal polishes and solid or liquid chemicals. On the other hand, metals will also corrode when being exposed to gaseous materials such as acid vapors, ammonia gas, formaldehyde gas and sulphur-containing gases (Roberge, 2007).

2.2 Concept in corrosion

In order for electrochemical corrosion to take place, the formation of a corrosion cell is essential where it comprised of the following components as illustrated in Figure 2.2 (Ahmad, 2006):

i. A metal anode.
ii. A metal cathode.
iii. A metallic conductor between the anode and cathode.
iv. An electrolyte which is water containing conductive salts in contact with the anode and cathode but not necessarily of the same composition.

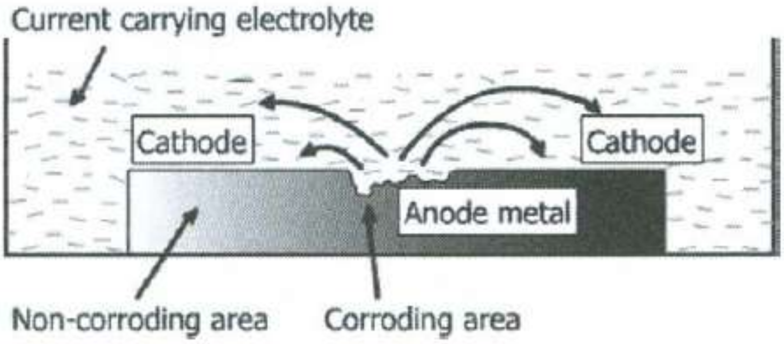

Figure 2.2 Corrosion cell in action.

Since corrosion mechanisms is complex and usually involve more than one definable steps with the rate of the overall reaction controlled by the slowest step due to the anodic dissolution reaction of metal that is likely to be balanced by the cathodic reaction during corrosion. The simplistic mechanism is shown in Figure 2.3. For the atmospheric corrosion of iron, some sites on the iron metal surface act as anodic facilitating oxidation.

Anodic reaction:

$$2Fe \rightarrow 2Fe^{2+} + 2e^- \qquad (2.1)$$

The oxygen present in the atmosphere is reduced at the cathodic site on the metal surface where the reduction process occurs.

Cathodic reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (2.2)$$

The overall corrosion process is:

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2\ (s) \qquad (2.3)$$

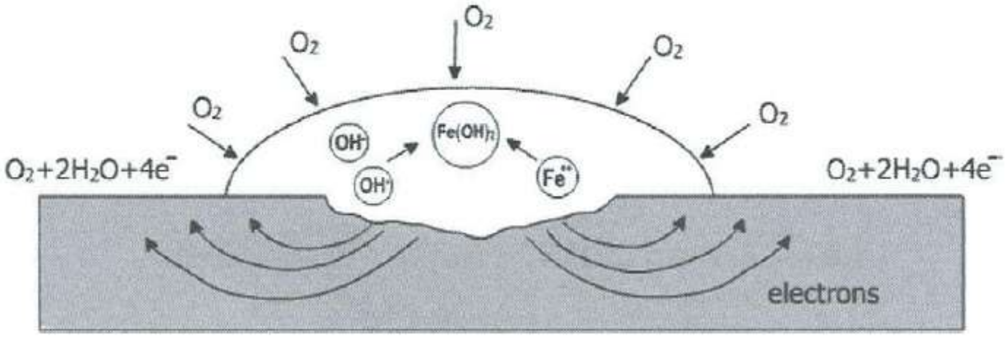

Figure 2.3 Electrochemical process involved in corrosion of iron (Ahmad, 2006).

In this electrochemical corrosion of iron, electrons are released at the anode to form the dissolved Fe^{2+} ions, whereas reduction takes place at the cathode which consumed electrons to form OH^- ions. When the solubility is exceeded, Fe^{2+} and OH^- combined to deposit iron (II) hydroxide solid, $Fe(OH)_2$ (s), which is sometimes called white rust. In the presence of oxygen and water, the unstable precipitate of $Fe(OH)_2$ can be easily oxidized by air or undergo hydrolysis to form various iron oxides and hydroxides (Ahmad, 2006).

2.3 Corrosion control and corrosion monitoring

It is impossible to completely prevent corrosion of most metals as they are thermodynamically unstable in the environment. We also cannot bear the staggering costs of corrosion that affect the national economy significantly, thus, corrosion monitoring and corrosion control methods must be adapted in order to combat these issues. Corrosion monitoring is carried out to predict the longevity of the structures and equipment. Corrosion monitoring methods are the control methods of corrosion situation, which is the control of metal behaviour under particular environmental conditions. There are three main factors that influence the corrosion process which are metal type, environment and conditions between metal-environment. Corrosion monitoring methods must provide the real time (immediate) information. The integration of corrosion monitoring in existing systems can thus supply early warning of costly corrosion destruction. Corrosion monitoring relates to preventive anti-corrosion measures where different techniques are used for corrosion control. On the other important note, corrosion control measures are taken to control or to keep in check the corrosion process. Corrosion monitoring and corrosion control relates to each other as corrosion monitoring provides us information on how to define and interpret the efficiency of the corrosion control methods. For instance, when corrosion monitoring is used to control corrosion like in testing the efficiency of inhibitors or studying the corrosion mechanisms to optimize the corrosion control. Thus, it is necessary that the corrosion mechanism and the corrosion rate at times of noncompliance be relatively known. Corrosion control methods include; (i) addition of inhibitors, (ii) the use of protective coatings, (iii) anodic protection, (iv) cathodic protection, (v) oxygen scavengers and (vi) impressed current protection with hope to prevent and to reduce the rate of corrosion to its lowest extent.

2.4 Corrosion inhibitors

Inhibition is a preventive measure against corrosive attack on metallic materials. Inhibitors are the general name for substances that are being present in small concentrations that may significantly reduce the rate of corrosion reactions, diminish growth in microbial corrosion and hinder the proceeding of physiological processes or even stop them. Inhibitors come from the Latin word “inhibire” meaning to hold, to suppress or to retain. Inhibitors are substances that work oppositely to catalysts by slowing down the reaction. Corrosion inhibitors are chemicals which when added in small concentrations to the environment, effectively suppressed the rate of corrosion to an acceptable level. The use of corrosion inhibitors are one of the most widespread methods of changing the chemistry of the environment. A corrosion inhibitor should not only mitigate corrosion, but also compatible with the environment.

Nowadays, intensive research has been carried out for the purpose to substitute toxic inhibitors for non-toxic or less toxic ones. However, there is no clear and accepted definition of “environmental friendly” or “green” corrosion inhibitors. Above all of the points stated, they must be assessed from the health, safety and environmental point of view. Corrosion inhibitors used must be low in toxicity or better to be non-toxic, low bioaccumulation, biodegradable and should not contain any harmful substances. A corrosion inhibitor can function in two ways. In some cases, the corrosion inhibitor can alter the corrosive environment into a non-corrosive or less corrosive environment through its interaction with the corrosive species. While in other cases, the corrosion inhibitor interacts with the metal surface and renders protection of the metals from corrosion (Sastri et al., 2007). There are two broad classes of inhibitors based on the mode of interaction; environment modifiers and adsorption inhibitors. In the case of environment modifiers, the action and the mechanism of inhibition is a simple interaction with the present aggresive species. For instance, the use of oxygen scavengers to inhibit the corrosion reaction. On the other hand, in the case of inhibitors which adsorb on the metal surface, there are two steps involved, namely the transport of the inhibitor to the metal surface and the metal-inhibitor interactions.

2.5 Adsorption in corrosion inhibition at the metal surface

It is widely accepted that corrosion inhibition is due to the adsorption of inhibitor molecule at the metal-solution interface, accompanied by a change in potential difference between the metal electrode and the solution as a result of non-uniform distribution of electric charges at the interface. The metal-solution interface is characterized by an electrical double layer and in a very rare case in triple layers. A schematic representation of the electrical double layer is given in Figure 2.4. The first layer at the metal surface is a sheet of charges caused by an excess or deficiency of electrons. The second layer which is the region A is formed on the solution side of the interface by specially adsorbed ions. The loci at the centres of these charges form the inner Helmholtz plane of the double layer. These anions lose their coordinated water molecules, displace adsorbed water molecules from the metal surface and in turn adsorbed on portions at the metal surface. These are the potential-determining ions and the charges are balanced by hydrated ions of opposite charge in the outer Helmholtz plane in region B, known as counterions. Region C is the Guoy-Chapman diffuse layer where the concentrations of the counterions decrease toward that of bulk electrolyte and function to balance the net charge close to the metal surface. Equation 2.4 may be written as:

$$M\,(nH_2O)_{(ads)} + I_{(sol)} \rightleftharpoons MI_{(ads)} + nH_2O_{(sol)} \qquad (2.4)$$

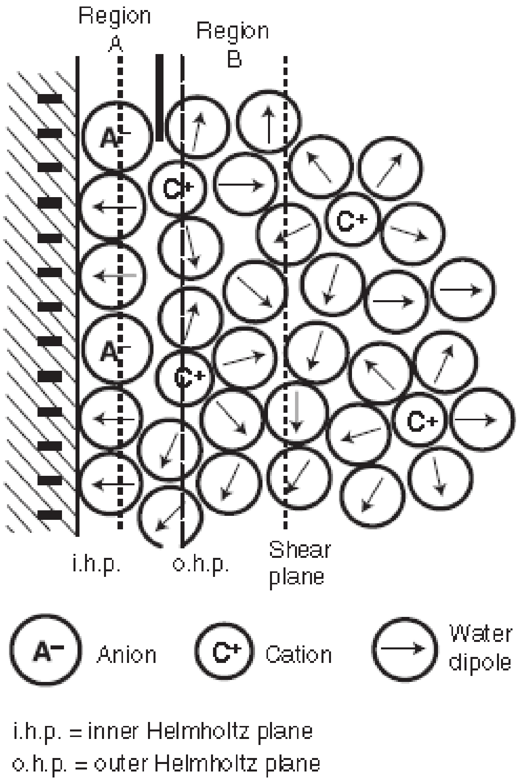

Figure 2.4 Schematic representation of an electrical double layer (Sastri, 2011).

I is inhibitor that approaches and adsorbs at the metal-solution interface. Inhibitor displaces *n* water molecules that are initially adsorbed on the metal. The adsorption of the inhibitor occurs as a result of the interaction energy between metal-inhibitor is more favorable than the interaction energy between metal-water molecules (Sastri et al., 2007).

The adsorption inhibitors have been classified as cathodic inhibitors, anodic inhibitors and mixed-type inhibitors which suppressed both cathodic and anodic reactions. Cathodic inhibitors inhibit cathodic reaction such as the hydrogen evolution in acidic solution or the reduction of oxygen in neutral or alkaline solution. Cathodic inhibitors do not cause local attack if their concentration is less than the amount needed for effective protection, in comparison to the anodic inhibitors, where, if added in insufficient concentrations, they may result in localized corrosion due to the increase in the ratio of cathodic to anodic surface (Groysman, 2010). Oxyanions such as chromates, molybdates and sodium nitrite are effective anodic inhibitors. These types of inhibitor are generally effective in the pH range of near neutral to basic. The corrosion current is reduced and the corrosion potential is shifted anodically (positively) for an anodic inhibitor and cathodically (negatively) for a cathodic inhibitor. In the case where the inhibitor affects both partial reactions, the shift in corrosion potential will depend on which is more dominant. Little or no potential shift may in fact occur. Most of the organic inhibitors comprise of active functional groups as they have the ability to bond to the surface of metal, thus, they are belonging to the mixed type inhibitors.

2.6 Classification of inhibitors

Classification of corrosion inhibitors is somewhat a subjective exercise, being very much dependent on the method employed. One can choose to classify them according to their chemical nature (organic or inorganic substances), their characteristics (oxidizing or non-oxidizing compounds) and their technical field of application whether in pickling, descaling, acid cleaning, cooling water systems, etc. (Schweitzer, 2007). Generally, inhibitors can be classified as passivating inhibitors, precipitation inhibitors, vapour phase inhibitors and organic inhibitors.

2.6.1 Passivating inhibitors

Passivating inhibitors are anodic inhibitors that shift largely the anodic potential in more positive (noble) direction, hence, forcing the metallic surface into the passivating range. These inhibitors deactivate anodic sites on the metal surface by causing the local current density to exceed the value needed for passivation. The passivating inhibitors are usually inorganic compounds that induce passivation on the metallic surfaces. They can be divided into two groups. The oxidizing anions such as chromate, nitrite and nitrate that can passivate on metallic surface in the absence of oxygen. Also, the non-oxidizing passivating inhibitors such as molybdates, phosphates and benzoates that may facilitate the adsorption of the oxygen in the molecules to passivate the metal surfaces. The passivating inhibitors are known to be the most effective and the most widely used type of inhibitors amongst all. The passivation process is illustrated in Figure 2.5. The passivating inhibitors slow down the corrosion process by several mechanisms (Bradford, 2006):

i. They stabilize the passive film, thus, reducing the corrosion rate.
ii. They repassivate the metal if the film is damaged.
iii. They assist in film repair, some of them forming an insoluble compounds that plug pores in the film.
iv. They prevent adsorption of aggressive anions like Cl^- by competitive adsorption of inhibitive anions.

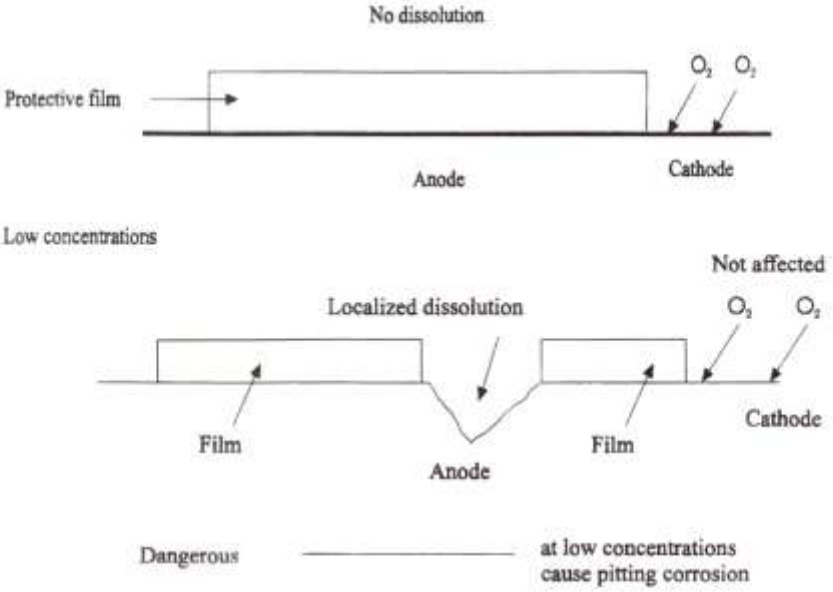

Figure 2.5 Passivating inhibitors (Sastri, 1998).

However, most of them pose a threat to human health as well as to the environment due to toxicity and detrimental effect they may bring to the surroundings. The concentration of inhibitors used is critical as at low concentration or when the concentration falls below its minimum limit, they may promote pitting and accelerate corrosion processes. For this reason, it is essential that constant monitoring of the inhibitor concentration be performed. Pitting is caused due to large cathode-to-anode surface areas when some active sites are not protected.

2.6.2 Precipitation inhibitors

Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal by forming a protective film. These inhibitors block both anodic and cathodic reaction by the formation of precipitates on the surface of the metal, thereby, providing a protective film. In near-neutral solution, metal surfaces are usually covered with oxides, hydroxides or salts present due to their reduced solubility in the region of corroding metal/solution interface. Here, a precipitation between cations of the corroding metal and the inhibitor deposits a three-dimensional barrier film on the metal surface. Such film is formed when the solubility product is exceeded for the salt formed between the cations of the metal and the anions of the inhibitor. Hard water which is high in calcium and magnesium is less corrosive than soft water due to the tendency of the salts in hard water to precipitate on the metal surface, hence forming a protective film. If the pH is adjusted to near neautral, this will lead to the formation of precipitate providing a protective film. The inhibition can be improved by the addition of zinc which suppress the cathodic reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{2.5}$$

This is often achieved by precipitation of an insoluble species onto cathodic sites forming a barrier preventing further O_2 reduction.

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow \tag{2.6}$$

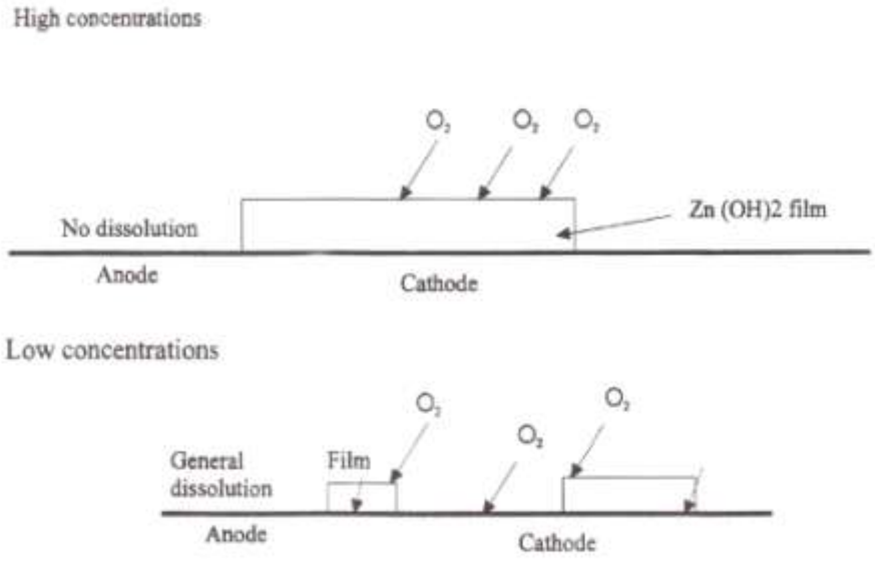

Figure 2.6 Precipitation inhibitors (Sastri, 1998).

2.6.3 Vapor phase inhibitors

These inhibitors are used to protect critical machined parts from corrosion during shipment and storage. Organic compounds with vapor phase in the range of 10^{-2} to 10^{-7} mmHg usually acts as good vapor phase inhibitors (Sastri, 1998). The inhibitor increases the atmospheric-corrosion resistance of the exposed metal surface and they are particularly useful in impeding atmospheric corrosion in gaseous atmospheres that contain moisture or other corrosive agents like Cl^-, H_2S and SO_2 (McCafferty, 2010). For instance, dicyclohexylamine nitrite and nitrobenzoate are usually applied on metallic surface by evaporating it from the source. Other examples include the use of vapor phase inhibitor to protect the metal surface as electronic equipment is sealed in a plastic sack with a slip of paper. Since vapor phase inhibitors are strongly depends on their vapor pressure properties, compounds bearing low vapor pressure are usually not suitable as inhibitors because they cannot form sufficient vapor needed to form “passive” layer.

2.6.4 Organic inhibitors

The need for organic inhibitors arises because of the awareness to environmental and health issues. These inhibitors are commonly used in acids, a few functions in neutral or alkaline solution. Essentially, the adsorption ability of organic inhibitors on the metal surface determine its inhibition efficiency by inhibiting the corrosion reactions. The adsorption may range from electrostatic attraction, interaction of the uncharged electron pairs in the molecule, interaction of the π electrons with the metal, or combination of any of them.

2.7 Inhibitor evaluation

Since there may be more than one inhibitor suitable for a specific application, it is therefore necessary to compare the performance of each. Besides simple test that based on pass or fail criterion using visual perception, there are a number of criteria that can be used. These include the measurements of weight loss and electrochemical methods that include potentiodynamic polarization measurement (Tafel method) and electrochemical impedance spectroscopy (EIS).

2.7.1 Weight loss measurement

Weight loss or also known as gravimetric is considered to be the simplest and the most widely method used both in laboratory and industry to study corrosion phenomenon. It gives useful information about the average corrosion rate over certain period of time. It is important that the surface of the coupon must be prepared carefully and the dimensions and initial weight of the coupons must be defined. The immersion time depends on the corrosiveness of the solution and coupon’s material. Colour identification of corrosion products formed on the surface of a coupon may provide preliminary information about the presence of species causing corrosion. The corrosion products should be removed for subsequent chemical identification. The surface of the coupon must be cleaned chemically or mechanically to decrease the loss of clean metal during chemical cleaning. The benefits of the weight loss method are:

i. The corrosion rate calculated is precise with 3-5% reproducibility. The reliability of this method is high. However, it is recommended to compare with other corrosion monitoring methods.
ii. It is possible to measure the corrosion rate of metals in any media and under wide process conditions.
iii. It is possible to examine a coupon’s surface and corrosion products, hence to identify the corrosion phenomenon and corrosion mechanism.

However, there are few limitations for this method:

i. In order to receive reliable data, in many cases, longer time is needed as corrosion rates may be calculated only after removal of a coupon from the system. For instance, if the corrosion rate is low, there is a need to wait for a longer period of time.
ii. The coupons provide general and average data about corrosion over a period of time. However, environmental conditions may vary every moment and it is impossible to know what happen in each upsets.
iii. This method is time consuming as we need to treat the coupons; to clean, to weigh and to take into account the cleaning factor.
iv. This method is not suitable for assessing corrosion of non-iron alloys, for instance, copper alloys in water as sensitivity and accuracy of weight loss for copper coupons are low in water in the presence of corrosion inhibitors.
v. It is not always suitable for the use in industry because of the difficulties of installation and the coupons have to be changed every month or every few months.
vi. This method does not permit real-time (on-line) monitoring.

2.7.2 Electrochemical methods

These methods are based on the established fact that the corrosion of metals and alloys in solution of electrolytes is generally an electrochemical process. This means that the electrochemical methods are only suitable for corrosion of metals in media with high electrical conductivity. Electrochemical reaction kinetics is essential in determining and explaining the corrosion rate of a metal exposed to a corrosive electrolyte. On the other hand, thermodynamics predicts the possibility of corrosion but it does not provide information on how fast or slow corrosion occurs. If the electrochemical system comprise of the electrode and electrolyte is in equilibrium, then, the net reaction rate is zero. Reaction rates are governed by chemical kinetics while corrosion rates are primarily governed by electrochemical kinetics.

2.7.2.1 Potentiodynamic polarization

Direct current (DC) electrochemistry and in particular, the potentiodynamic polarization measurement allows considerable information on electrode processes. Through this measurement, information on the pitting susceptibility, corrosion rate, passivity as well as the cathodic behavior of an electrochemical system may be known. Based on the points previously mentioned above, electrochemical kinetics of a corroding metal can be characterized by three polarization parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}) and Tafel slopes (β_a and β_c) which may be obtain from the E-i relationship of metal. This is an accelerated electrochemical process for determining the corrosion rate that has an advantage over