EFFECT OF ARECA CATECHU EXTRACTS AS GREEN CORROSION INHIBITOR ON CONCRETE PROPERTIES

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To My Parents

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For their patience, support, love, and for enduring the ups and downs during the completion of this thesis.

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ABSTRACT

The most significant reason of failure in reinforced concrete structure worldwide is corrosion of reinforcement. Presently a great tendency has been shown on preventing reinforcement corrosion by means of corrosion inhibitors. In addition, studying the effects of inhibitors on concrete properties despite of corrosion aspect could have significant impact on engineering use of them. Therefore, the aim of the present research was to evaluate the performance of environment friendly green plant namely, Areca Catechu extracts inhibitor additions to contaminated concrete containing 5% magnesium sulphate and sodium chloride with water cement ratio of 0.55 in simulated tropical climate. Areca Catechu (Areca Catechu leaf extracts) inhibitor was selected through screening of five green plants extracts, namely; Acacia Longifolia (Acacia), Areca Catechu (Areca Palm), Elastoma Malabathricum (Indian rhododendron), Elaeis Guineensis (Oil Palm) and Cocos Nucifera (Coconut), and two chemical commercial inhibitor namely, Triethanolamine and natrium nitrit. As a result, Areca Catechu was selected due to its high efficiency and high content of potassium. Accordingly, Areca Catechu effectiveness as green inhibitor was compared to natrium nitrit as chemical inhibitor. The specimens were subjected to various tests in order to study fresh, physical, mechanical, chemical, permeability, durability and microstructural properties of contaminated and inhibitor-added concrete. From the results, Areca Catechu exhibited high inhibition efficiency and acceptable adsorption characteristics. In addition, the green inhibitor-added concrete produced acceptable compressive, tensile and flexural strength, low permeability proved by water absorption and ISAT test, and exhibited lowest corrosion rate, lowest double layer capacitance (C_{dl}), highest concrete resistivity and also highest polarization resistance (R_p) values for the entire period of exposure, compared to natrium nitrit. In conclusion, Areca Catechu exhibited a good substitute for chemical and toxic corrosion inhibiting admixtures for durable concrete constructions due to its hydrophobic effects, availability, viability, versatility and eco-friendliness.

ABSTRAK

Punca utama kegagalan struktur konkrit tetulang secara global adalah kakisan tetulang. Dewasa ini, terdapat kecenderungan yang tinggi yang menunjukkan kakisan tetulang boleh dicegah dengan penggunaan perencatan kakisan. Selain itu, adalah penting kesan perencat terhadap sifat-sifat konkrit diambil kira selain aspek kakisan untuk kegunaan industri dan kejuruteraan. Oleh itu, kajian ini bertujuan untuk mengenal pasti prestasi ekstrak tumbuhan hijau mesra alam, iaitu Areca Catechu sebagai perencat yang ditambah pada konkrit tercemar yang mengandungi 5% magnesium sulfat dan natrium klorida dengan nisbah air kepada simen ialah 0.55 disimulasikan dengan iklim tropika. Perencat Areca Catechu (ekstrak daun Areca Catechu) dipilih melalui saringan lima ekstrak tumbuhan hijau dan dua perencat kimia komersial iaitu Acacia Longifolia (Acacia), Areca Catechu (Areca Palm), Elastoma Malabathricum (Indian rhododendron), Elaeis Guineensis (Oil Palm) dan Cocos Nucifera (Kelapa), Triethanolamine dan sodium nitrite. Hasilnya, Areca Catechu telah dipilih kerana kecekapan dan kandungan potassium yang tinggi. Dengan yang demikian, keberkesanan Areca Catechu sebagai perencat semula jadi dibandingkan dengan natrium nitrit sebagai perencat kimia. Spesimen-spesimen konkrit tercemar yang ditambah perencat diuji dengan pelbagai ujian, iaitu ujian konkrit segar, fizikal, mekanikal, kimia, ketelapan, ketahanlasakan, dan sifat-sifat mikrostruktur. Hasil daripada itu, Areca Catechu menunjukkan kecekapan perencatan yang paling tinggi kecekapannya dan ciri-ciri penyerapan yang dibenarkan. Selain itu, penambahan perencat ini di dalam konkrit menunjukkan kekuatan mampatan, kekuatan ketegangan dan kekuatan lenturan yang memuaskan. Sifat ketelapan air yang rendah dibuktikan melalui uji kaji penyerapan air dan ujian permulaan penyerapan permukaan (ISAT). Manakala dari aspek kakisan, penambahan perencat ke dalam konkrit menunjukkan kadar kakisan yang rendah, kapasiti dwi-lapisan (Cdl) yang rendah, konkrit rintangan yang tinggi dan juga nilai rintangan polarizasi (Rp) yang tinggi sepanjang tempoh pendedahan berbanding natrium nitrit. Kesimpulannya, Areca Catechu boleh dicadangkan sebagai pengganti yang baik kepada perencat kakisan kimia dan toksik untuk ketahanlasakan pembinaan konkrit kerana kesan hidrofobik, ketersediaan, daya maju, serba boleh dan, mesra alam.

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LIST OF ABBREVIATIONS

AAS	-	Atomic absorption spectroscopy
ABT	-	2-aminobenzothia-zole
AC	-	Areca Catechu
ACI	-	American concrete institute
AEA	-	Air entraining admixture
AL	-	Acacia longifolia
AMA	-	Aminoalcohols
AMN	-	2-amino-4-(4-methoxyphenyl)-6-phenylnicotinonitrile
AOAC	-	Association of official analytical chemists
ASTM	-	American society for testing and materials
ATN	-	2-amino-6-phenyl-4-(p-tolyl)
BK	-	Bark
BS	-	British standards
CE	-	Counter electrode
CI2C	-	2% chemical inhibitor-added concrete
CN	-	Cocos nucifera
CNI	-	Calcium nitrite inhibitor
CP	-	Cathodic protection
CPrev	-	Cathodic prevention
DEA	-	Diethanolamine
DHP	-	Disodium hydrogen phosphate

DMEA	-	Dimethylethanolamine
DSS	-	Disodium tetrapropenyl succinate
ECE	-	Electrochemical chloride extraction
EDX	-	Energy-dispersive X-ray spectroscopy
EG	-	Elaeis Guineensis
EIS	-	Electrochemical impedance spectroscopy
FBEC	-	Fusion bonded epoxy coated
FESEM	-	Field emission scanning electron microscopy
FHLE	-	Ficus hispida leaves extraction
GI2C	-	2% green inhibitor-added concrete
IBD	-	Institute of bio-product development
IE	-	Inhibition efficiency
ISAT	-	Initial surface absorption test
ISO	-	International standard organization
ITZ	-	Interfacial transition zone
LPR	-	Linear polarization resistance
LV	-	Leaves
MBT	-	2-mercaptobenzothiazole
MCI	-	Migrating corrosion inhibitor
MEA	-	Monoethanolamine
MFP	-	monofluorophosphate
MM	-	Melastoma Malabathricum
MN5C	-	5% magensium sulphate and sodium chloride added concrete
OPC	-	Ordinary Portland cement
pH	-	Alkali or acidity level
PPM	-	Part per million
RE	-	Reference electrode

RH	-	Relative humidity
RT	-	Roots
SCC	-	Self-compacting concrete
SCE	-	Saturated calomel electrode
SCPS	-	Simulated concrete pore solution
SDP	-	Strength deterioration percentage
SEM	-	Scanning electron microscopy
SN	-	Sodium nitrite
TEA	-	Triethanolamine
TSP	-	Trisodium phosphate
UPV	-	Ultrasonic pulse velocity
UTM	-	Universiti Teknologi Malaysia
WE	-	Working electrode
XG	-	Xanthan gum
XRF	-	X-ray Flourescence

LIST OF SYMBOLS

A	-	Cross section area of specimen (mm^2)
a	-	Atomic weight of iron (g/mol)
B	-	Tafel constant
C	-	Concentration of inhibitor
D	-	Density of steel (g/cm^3)
F	-	Maximum load at failure (Pa)
H	-	Hydrogen
K	-	Constant
L	-	Distance between transducers (m)
n	-	Number of electrons exchanged in corrosion reaction
O	-	Oxygen
T	-	Temperature
T	-	Effective time for transit (s)
T	-	Time of exposure (hours)
V	-	Ultrasonic pulse velocity (m/s)
W	-	Weight loss in the presence of the inhibitor
ρ	-	Resistivity
Ca	-	Calcium
Cl	-	Chlorine
Fe	-	Iron
HCl	-	Hydrogen chloride

IE	-	Inhibition efficiency
KHz	-	Kilohertz
KOH	-	Potassium hydroxide
MHz	-	Megahertz
MPa	-	Mega pascal
v/v	-	Volume per volume
Θ	-	Degree of surface coverage
$Z(\omega)$	-	Frequency dependent impedance
$Z''(\omega)$	-	Imaginary impedance
$Z'(\omega)$	-	Real impedance
ΔW	-	Average weight loss
γ-FeOOH	-	Lepidocrocite
α-FeOOH	-	Goethite
C-S-H	-	Calcium silicate hydrate
W/C	-	Water to cement retio
Cl^-/OH^-	-	Chloride to hydroxyl ionic concentration
AFt	-	Ettringite
NaCl	-	Sodium chloride
R^2	-	Goodness of fit
$\Delta G^o{}_{ads}$	-	Adsorption energy
σ_{max}	-	Maximum stress
$3Ca.Al_2O_3.3CaSO_4.31H_2O$	-	Calcium sulfoaluminate
$3CaO.Al_2O_3.12H_2O$	-	Calcium aluminate hydrate
Al_2O_3	-	Alumina
b_a	-	Anodic tafel slope
b_c	-	Cathodic tafel slope

C_3A	-	Tricalcium aluminate
$C_3A.CaCl_2.10H_2O$	-	Chloroaluminate
$Ca(NO_2)_2$	-	Calcium nitrite
$Ca(OH)_2$	-	Calcium hydoxide
$Ca(OH)_2$	-	Potlandite
CaO	-	Calcium oxide
C_{dl}	-	Double layer capacitance
CO_2	-	Carbon dioxide
CO_3	-	Carbonate
CP_1	-	Specific heat capacity of water
CP_2	-	Specific heat capacity of concrete
$CuSO_4$	-	Copper sulphate
d_1, d_2	-	Lateral dimension of the specimen (mm)
EC_{50}	-	50% effective concentration
E_{corr}	-	Corrosion potential
E_p	-	Predictive modulus of elasticity
E_s	-	Experimental modulus of elasticity
F_c	-	Compressive strength (Mega pascal)
f_c	-	Compressive strength (MPa)
F_{ca}	-	Average of compressive strength for the specimen after immersion in sulphate solution
F_{cf}	-	Flexural strength (Mega pascal)
f_{cf}	-	Flexural strength (MPa)
F_{ct}	-	Tensile strength (Mega pascal)
f_{ct}	-	Splitting strength (MPa)
f_{cy}	-	Maximum load of fracture
F_{cw}	-	Average of compressive strength for companion specimen cured in water

$Fe(OH)_2$	-	Iron hydroxide
Fe_2O_3	-	Hematite
Fe_2O_3	-	Ferric oxide
Fe_2O_3	-	Hematite
Fe_3O_4	-	Magnetite
Fe_3O_4	-	Magnetite
F_{max}	-	Maximum frequency
H_2SO_4	-	Sulphuric acid
H_d	-	Hardened density (kg/m^3)
H_{hyd}	-	Total heat of hydration of the cement
I_{corr}	-	Corrosion density
K_2SO_4	-	Potassium sulphate
LC_{50}	-	50% lethal concentration
Li_2MoO_4	-	Lithium molybdate
$LiCrO_4$	-	Lithium chromate
$LiNO_3$	-	Lithium nitrate
l_r	-	Distance between the lower roller (mm)
M_1	-	Weight of water
M_2	-	Weight of concrete
$Mg(OH)_2$	-	Brucite
MgO	-	Magnesium oxide
$MgSO_4$	-	Magnesium sulphate
$M\text{-}S\text{-}H$	-	Magnesium silicate hydrate
Na_2PO_3F	-	Sodium monofluorophosphate
$NaHPO_4$	-	Disodium hydrate phosphate
$NaNO_2$	-	Sodium nitrite
$NaSO_4$	-	Sodium sulphate

p_i	-	Weight ratio of i-th compound
R_c	-	Concrete resistance
R_{ct}	-	Apparent polarizing resistance
R_p	-	Polarization resistance
SiO_2	-	Silica
$Si\text{-}O\text{-}Al$	-	Aluminosilicate
SO_3	-	Sulphur trioxide
T_1	-	Temperature changes for water
T_2	-	Temperature changes for concrete
U_w	-	Unit weight (gram)
W_d	-	Dry specimen weight (kg)
W_o	-	Weight loss in the absence of the inhibitor
W_w	-	Wet specimen weight (kg)

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Concrete is the most popular material used in construction. It has high compressive strength so it can be used in any structure. Concrete lacks tension stress due to the bond between the cured cement and the surfaces of the aggregate. Thus, concrete is frequently reinforced with steel to compensate for its lack of tensile strength. Reinforced concrete is created when steel bars or a steel mesh is implanted into a concrete structure so that the steel can support most of the tensile stress. The corrosion of steel reinforcement in concrete is a worldwide phenomenon that should be considered by engineers prior to design and construction. Corrosion can cause serious economic and safety issues in construction. (Larsen, 2008; Fernandez et al., 2015).

Environmental exposure can cause corrosion of materials in concrete resulting in the deterioration of the structure. This is a critical issue that must be addressed for safety, environment and economic reasons (Chowdhury, 2004; Aguirre-guerrero et al., 2016). Metals are the most important materials used for structural and decorative utility. Although corrosion is a controllable process, it is an unavoidable phenomenon resulting in the deterioration or destruction of metals. The corrosion of metals acts like natural disasters in terms of negative impact on the economy and development of a country. Economic loss due to the corrosion of metals costs approximately $267 billion annually in the United States of America. This is much greater than loss due to the natural disasters, which is $17 billion per year. Optimum corrosion management practices have been suggested to save about 25-30% of annual loss due to metallic corrosion (Znini et al., 2012; Ji et al., 2015).

Penetration of chloride ions and carbon dioxide to the steel surfaces is the main reason for corrosion initiation of reinforcing steel in reinforced concrete. The corrosion products are usually iron oxides and hydroxides placed in a restricted area around the reinforcing steel after the corrosion process initiates. This process can produce expansive stresses that results in the cracking and spalling of the concrete cover. Crack and spall in concrete covers gradually results in the progressive deterioration of the concrete (Ahmad, 2003; Bardal, 2004; Qiao et al., 2015). Equations (1.1) to (1.5) show the chloride corrosive attack.

$$Fe \rightarrow Fe^{2+} + 2e^{-} \tag{1.1}$$

$$Fe^{2+} + 2Cl^{-} \rightarrow FeCl_2 \tag{1.2}$$

$$1/2O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \tag{1.3}$$

$$Fe^{2+} + 2\,OH^{-} \rightarrow Fe(OH)_2 \tag{1.4}$$

$$2\,Fe(OH)_2 + 1/2O_2 \rightarrow Fe_2O_3 + 2\,H_2O \tag{1.5}$$

A basic rule for chloride ions penetration is that chloride ions penetrate the passive oxide film of the reinforcement and combine with iron ions to form a soluble iron chloride complex. Iron can later be carried into the concrete for later oxidation process. Corrosion starts when chlorides reach a level of 0.15% (water-soluble chloride by mass of cement) in the concrete. The exposure of concrete to chloride could be from many sources such as chloride containing set accelerators, deicing salts, seawater, and airborne salts.

Carbonation is known as a cause of corrosion of steel bars. Carbonation corrosion reduces the alkalinity of concrete. Carbonation occurs as a reaction of atmospheric carbon dioxide with calcium hydroxide in the cement paste. The result of carbonation is a degeneration of calcium hydroxide to calcium carbonate which has low alkalinity, making it unable to support the passive oxide layer. The conversion of calcium hydroxide to calcium carbonate is shown in Equation (1.6), (Khan and Siddique, 2011; Song and Kwon, 2007; Shi et al., 2016)

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{1.6}$$

The carbonation reaction lowers pH. The protective oxide layer is lost and the corrosion process begins as the pH of the concrete around the embedded reinforcing steel drops below 12 (Khan and Siddique, 2011).

The presence of oxygen causes oxidation and reduction reactions at the steel-concrete interface, which is shown in Equations (1.7) and (1.8),

$$2Fe \rightarrow 2Fe^{2+} + 4e^{-} \tag{1.7}$$

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \tag{1.8}$$

Equation (1.7) shows the anodic reaction. In the anodic reaction, the iron is oxidized while releasing electrons and ferrous ions that dissolve in the solution around the steel. The electrons are placed on the steels' surface, lowering its potential. Equation (1.8) depicts the cathodic side, or reduction reaction. After the electrons released from the anodic reaction flow towards a higher potential on the cathodic side, they combine with water and oxygen molecules to form hydroxyl ions. The corrosion reaction continues owing to the presence of a cathodic reaction to accept released electrons. Producing procedure of different types of corrosion product is seen in Equations (1.9) to (1.12).

$$3Fe + 4H_2O \rightarrow Fe_3O_4 + 8H^{+} + 8e^{-} \tag{1.9}$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^{+} + 6e^{-} \tag{1.10}$$

$$Fe + 2H_2O \rightarrow HFeO_2^{-} + 3H^{+} + 2e^{-} \tag{1.11}$$

$$Fe \rightarrow Fe_2^{+} + 2e^{-} \tag{1.12}$$

The corrosion procedure can be stopped if there is no oxygen and water at the cathodic sites of the steel. (Duquette et al, 2011; Shi et al., 2016).

1.2 Background of Problem

Corrosion prevention expenses carried out during design are significantly lower than the compared cost of treatment during service life. The numeric example of the mentioned fact is as follows. Elsener et al. (2004) and Zhu et al. (2016) reported that expenses after finishing construction are 5 times greater than the corresponding expenses during the design period. In a same manner, the cost of construction is 25 times greater at the time when the corrosion has not started yet, while it is 125 times greater when the corrosion becomes widespread in comparison to corresponding expenses at design period. There are several methods of corrosion protection. Some of them are as follows (Wilmot, 2007; Daflou et al, 2000):

(a) Membrane-type coatings applied to the surface of concrete structures

(b) Painting the outer concrete surface to provide obstacle protection

(c) Using corrosion inhibitors in concrete

(d) Corrosion resistant metals are acceptable substitute for normal carbon steel reinforcement

(e) Cathodic protection of steel bars.

(f) Use of a coating on the reinforcement itself, i.e. epoxy coatings and specifically zinc in the form of hot dip galvanizing.

Corrosion inhibitors are chemical admixtures added in very small concentrations to concrete during batching as a corrosion-protection measure. Inhibitors are regularly used in low-permeability concrete. Inhibitors are corrosion reducers, not preventers. Thus, inhibitors may reduce the subsequent corrosion rate after corrosion initiates, which eventually lead to less corrosion-induced concrete deterioration. There are three major concerns that need to be considered for corrosion inhibitors. The first is the long-term stability and performance of the inhibitor. The second is how the inhibitor can affect corrosion propagation after corrosion starts. The third is the evaluation of inhibitor performance and its effect on concrete properties during construction service life (Al Zubaidy and Al Tamimi, 2012; Gartner and Kosec, 2016).

Corrosion inhibitors are categorized as inorganic or organic based on their chemistry mechanism. Organic inhibitors generally have heteroatoms. O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitor. There are 3 ways of protection by inhibitors, which affect the anodic reaction, the cathodic reaction, or both reactions. The first mechanism is to facilitate the formation of an oxide film on the surface of the steel reinforcing bars, which is active. The second mechanism is reduce the rate of chloride ion migration which is passive (Chambers et al., 2014).

Among the various organic compounds, there is a major tendency for the inhibitors to be nontoxic rather than the chemical and toxic inhibitors selected through industrial testing and research. Toxicity is the degree to which a substance can damage an organism. Toxicity of an inhibitor must be measured as both by LC_{50} and EC_{50}, while LC_{50} refers to the "lethal concentration" to affect (actually kill) 50% of the population and EC_{50} refers to the "effective concentration" of the chemical required to adversely affect 50% of the population. In general, EC_{50} values that represent concentrations required to stunt growth are lower than the LC_{50} values representing the 50% of lethal concentrations. Table 1.1 shows a number of publications on corrosion inhibitors (Vyrides et al, 2013).

Table 1.1: Publications amount related to corrosion inhibitors (Znini, 2012)

Decades	**Publications amount**
1951 to 1960	29
1961 to 1970	1235
1971 to 1980	1711
1981 to 1990	2685
1991 to 2000	4819
2001 to 2011	9873

Green inhibitors are non-toxic admixtures that are derived from natural resources specially plants. Green inhibitors are categorized into organic and inorganic green inhibitors (Znini, 2012). Organic green inhibitors are normally alkaloids, flavonoids, and other natural products from natural sources like plants. Synthetic compounds with negligible toxicity could also be categorized in this group (Rani and Basu, 2012; Nathiya and Raj, 2016). Table 1.2 shows some plants used in order to inhibit the corrosion of steel.

Table 1.2: Examples of Green Inhibitors used for corrosion inhibition of steel (Rani and Basu, 2012)

No.	Type of Metal	Source of inhibitor
1	Steel	Tea leaves
2	Steel	Pomegranate juice and Peels
3	Steel	Eucalyptus oil
4	Steel	Terminalia bellerica
5	Steel	Eucalyptus oil
6	Mild steel	Gum exudate
7	Mild steel	Banana peels
8	Steel	Natural amino acids
9	Steel	Aloe leaves
10	Steel	Mango/orange peels
11	Mild steel	Garcinia kola seed
12	Steel	Auforpio turkiale
13	Steel	Azydracta indica
14	C-steel	Lawsonia extract (Henna)
15	Steel	Emblica officinalis
16	Steel bar	Bambusa Arundinacea
17	Mild steel	Black pepper
18	Mild steel	Kopsia Singapurensis

In the last 20 years, there has been a worldwide tendency to investigate green corrosion inhibitors to create available, cheap, eco-friendly, nontoxic and effective molecules with low environmental impact (Buchweishaija, 2008; Kesavan at al, 2012; Rani and Basu, 2012; Sangeetha and Rajendran, 2011; Shahid, 2011; Zhao et al, 2010; Singh et al., 2016; Mehdipour et al., 2015; Bhawsar et al., 2015). Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Many plant extractions have been used as green inhibitors. Inhibitors affect concrete properties while creating chemical stability and preserving characteristics.

1.3 Problem Statement

One of the methods to prevent corrosion is to use corrosion inhibitors. However, there is a concern about the safety and environmental impact of using corrosion inhibitors. Organic and inorganic based inhibitors have been used to inhibit the corrosion of metals in constructions but are not easy to manufacture in some countries, as well as being toxic to the environment, which compromises sustainability efforts. Most of compounds and chemicals that have been tried as corrosion inhibitors are not environmentally friendly and are too expensive (Asipita et al., 2014). The mentioned inhibitors may cause temporary or permanent damage to human organ such as kidney or liver. The dangerous impact of synthetic inhibitors is obvious to the global community and there has been an environmental effort to replace these toxic and harmful inhibitors with green ones.

Plant extracts are an extraordinarily rich source of naturally synthesized chemical compounds that can be extracted by simple processes with low costs. Plant extracts and oils are highly efficient, non-toxic, renewable and cheap. The most important advantage of natural compounds as inhibitor is their biodegradable nature. These organic compounds reduce the corrosion rate by being absorbed into the metals surface and blocking active sites. The results of several studies show that plant extracts and oils have an inhibition efficiency of up to 98 percent. It is obvious that plant extracts and oils are effective corrosion inhibitors and can be positively used on an industrial level.

Several plants as corrosion inhibitors were investigated by many researchers who contributed to their green justification (El-Etre et al., 2005; Rajalakshmi et al., 2008; Eddy et al., 2010; Ashassi-sorkhabi et al., 2015; Mobin and Rizvi, 2016). There are few studies focused on the inhibitive effect of plants extracts on the corrosion of reinforcement in concrete (Asipita et al., 2014; Esah et al., 2013; Quraishi et al., 2012; Quraishi et al., 2011). There is no significant focus on investigating the effect of green inhibitors on concrete properties. As inhibitors affect concrete properties while creating chemical stability and preserving the characteristics for concrete, their effect on concrete properties should be determined. Although many green inhibitors may show satisfactory inhibition efficiency, it is obvious that only the green inhibitors which are capable of preserving concrete properties should be used in concrete to decrease concrete corrosion. However, no previous work to explore the Areca Catechu as a green corrosion inhibitor in reinforced concrete. In conclusion, aim of current research is to answer the following question:

Is it possible to apply Areca Catechu as a green corrosion inhibitor in contaminated concrete in order to decrease corrosion rate while preserve or improve concrete properties?

1.4 Aims and Objectives of Study

This study investigates the effect of green corrosion inhibitors on the engineering properties of reinforced concrete.

The specific objectives are as follows:

i. To evaluate the inhibitory performance of various leaf extracts as green inhibitors from *Acacia Longifolia* (Acacia), *Areca Catechu* (Areca Palm), *Elastoma Malabathricum* (Indian rhododendron), *Elaeis Guineensis* (Oil Palm) and *Cocos Nucifera* (Coconut) on mild steel.

ii. To determine the optimum percentage for the selected green inhibitor in terms of corrosion inhibition and concrete mechanical properties.

iii. To investigate the performance of selected green inhibitors on the physical and mechanical properties of concrete.

iv. To study the effect of the selected green inhibitors on the durability and microstructure properties of reinforced concrete.

1.5 Research Hypothesis

Non-polar green corrosion inhibitors can be used as an admixture to inhibit the corrosion of steel reinforcement in concrete attacked by a corrosive medium such as chloride, sulphate and carbon dioxide. Additionally, they may improve concrete properties regarding chemical components containing alkali metals and functional group of nitrogen. It is hypothesized that Areca Catechu (shown in Figure 1.1) could be an alternative green inhibitor in the future for reinforced concrete structures.

Figure 1.1 Areca Catechu tree and leaves

1.6 Scope and Limitations of Study

This study is related to Green corrosion inhibitors involving laboratory experimentation to determine the inhibitory effects of green corrosion inhibitors on the durability and mechanical properties of reinforced concrete structures in a simulated tropical climate.

This study investigates whether or not green corrosion inhibitors can preserve concrete properties and inhibit the corrosion of reinforcement in reinforced concrete structures. Some terms and limitation of this study are as follows:

a) 'Contaminated concrete' is referred to concrete which is tainted with impurities or aggressive agents.

b) 'Performance' is a term associated to the comparative observation between control sample and the one added with inhibitor.

c) 'Green inhibitors' are referred to non-toxic admixtures that are derived from natural resources specially plants.

d) 'Toxicity' is the degree to which a substance can damage an organism.

e) 'Inhibition efficiency' is defined as difference in weight loss or corrosion rate values in presence and absence of inhibitor.

f) 'Concrete properties' is defined as fresh, mechanical, physical, permeability, durability and microstructure behavior of concrete.

g) Leaves extract will be used as additive materials.

h) Water binder ratio is limited to 0.55 ($\frac{w}{c}$ = 0.55).

i) One type of cement (OPC) is used.

j) The curing periods varies from 3 days to 6 months depending on the test.

k) Time duration was limited to three (3) years and the maximum exposure time for testing was 360 days.

l) Fresh properties of green inhibitors added to concrete were measured by the workability and compatibility criteria of concrete such as slump, fresh density.

m) Mechanical properties of green inhibitors added to concrete were measured using compressive strength, tensile strength and flexural strength, modulus of elasticity, and ultrasonic pulse velocity.

n) Durability properties of green inhibitors added concrete were measured using heat of hydration, specific heat capacity, acid attack, accelerated carbonation, and corrosion test.

o) Standards, material, methods for testing were all based on ASTM, BS and BS EN Standards.

p) The effect of chloride and Sulfate attack was determined using the EIS, LPR, Tafel methods and comparing weight loss results.

1.7 Significance of the study

Many countries are affected by the corrosion of reinforced concrete structures and its disadvantages, so studying inhibitors is very important. Since many corrosion inhibitors are used in reinforced concrete structures to inhibit the corrosion of concrete reinforcement, it is necessary to know their effects on concrete properties, as they can improve, preserve or worsen concrete properties.

This study’s significance is:

a) To produce concrete structures without corrosion side effects.

b) To introduce new plant extract to be used as green corrosion inhibitor.

c) To use eco-friendly and non-toxic inhibitors to avoid the environmental pollution made by chemical inhibitors.

d) To improve concrete properties in terms of corrosion.

e) To reduce the life cycle cost of concrete structures.

f) To increase the life-time service of reinforced concrete structures.

g) This study’s findings contribute to the application of new green corrosion inhibitors to preserve concrete properties while decreasing corrosion rates.

1.8 Thesis Organization

This thesis was organized according to the UTM thesis manual 2015, which defines introductory pages, text, references, background and report sections. Therefore, this thesis was designed to consist of seven chapters.

Chapter one: Provides a general description of the background problem. This chapter also describes the aims and objectives, scope and limitation, research hypothesis, research significance and thesis layout.

Chapter two: Presents detailed information on corrosion steel reinforcement in concrete and explanations of past research on corrosion. A review of state-of-the-art corrosion basics, corrosion mechanism, corrosion factors, and corrosion prevention methods is discussed. A classification of corrosion inhibitors, corrosion inhibitors effects on the corrosion inhibition of mild steel and concrete properties is provided. A critical review is provided as a conclusion.

Chapter three: The materials, methodology, standards, and test modifications are described in this chapter. This chapter describes the experimental investigations for the behavior of the materials used and the procedures for determining the fresh and hardened properties of concrete. All tests are cited to the following references; British Standards (BS) and American Standards for Testing Material (ASTM).

Chapter four: This chapter reveals the result of the mild steel corrosion test done in order to achieve the first objective of the research. It was mainly conducted through screenings of various green plant extracts at the Institute of Bio product Development (IBD) and Chemistry department of Science faculty, both of which are in UTM. Chemical analysis and green plant extract inhibition efficiencies are provided in this chapter. The results for the optimum percentage of green inhibitor are shown. The first two objectives of this research are presented in this chapter.

Chapter five: This chapter consists of the results on the effect of green corrosion inhibitors on the physical and mechanical properties of magnesium sulphate and sodium chloride contaminated concrete. Aspects of physical and mechanical performance covered in this chapter are slump, fresh density, pH measurements, compressive strength, tensile strength, flexural strength, Ultrasonic Pulse Velocity (UPV), and modulus of elasticity, water adsorption test, Initial Surface Adsorption Test (ISAT), heat of hydration test, specific heat capacity, .

Chapter six: This chapter deals with the results for permeability, durability and microstructure properties of magnesium sulphate and sodium chloride contaminated concrete in the presence of green corrosion inhibitor. The results of sulphate resistance, acid attack test, accelerated carbonation test, Field Emission Scanning Electron Microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDX) are presented. Corrosion tests consisting of Electrochemical Impedance Spectrometry (EIS), Linear Polarization resistance (LPR), Tafel, and gravimetric (Weight Loss) tests are presented in this chapter.

Chapter seven: This chapter concludes the thesis by stating the findings and achievements of the study and contributions to existing knowledge. Recommendations are made for further research in similar areas.

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