Efficacy of Corrosion phenomena, challenges and control in steel industry: An overview

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Abstract:
The mitigation of corrosion is a major problem for many industries all over the world as it is costly to maintain metals especially in all energy sectors. There are different methods been used such as painting, coating and galvanizing; but, all these solutions are relatively expensive and cause harmful effect to the environment. It is pertinent to develop and apply emerging technology that will yield high resistance to corrosion, as a way of controlling corrosion in order to reduce corrosion cost, lower the risk of failure, accidents and extend the useful lives of equipment and building. This foster the search of natural plants with green inhibitors which are eco-friendly and relatively inexpensive. This paper investigates the corrosion mechanism process and possible mitigation in steel application.

Keywords: Corrosion; Mild steel; Environment; Industries

1. Introduction
Metal degradation and corrosion are issues that cannot be disregarded when considering the utilisation of metal in our society. This destructive effect has been seen when the metal in the combined state tends to revert to its most stable natural state on exposure to certain environmental conditions. This effect of corrosion transition has drastically and technically affected several industries resulting in losses and damages with a large deficit [1]. A huge loss of investment has been incurred as a result of metallic corrosion and degradation, an estimated value of 276 United States dollar (USD) equivalent to 3.1 per cent of the United States Gross domestic product (GDP) was estimated in the past [2]. Corrosion of metals is confronted with several challenges such as decrease in yield, ductility, ultimate strength, downtime of a running plants, collapsed constructions resulting in devastating consequence [3]. Corrosion has been a destructive phenomenon that affects almost all metals. Hence, corrosion inhibitor serves as a constructive organic phenomenon that can prevent or combat the depletion of the metal surface. This has proven to be very successful, mostly in energy sectors [4]. Phytochemical constituents such as alkaloids, flavonoids, and tannins have also been investigated through phytochemical screening and corrosion techniques to be efficient inhibitor molecule [5]. Availability and stability of the inhibitors in the market must be considered for their proper selection and applications. The toxicological activity of most synthetic compounds reveals high adverse health effect on human and biota with respect to exposure period [1]. This foster scientific recognition to develop more effective, environmentally friendly or natural product corrosion inhibitors called “green inhibitor” due to their availability, renewability, cost-effectiveness and ecological source of materials [6]. Prevention approach is of great necessity in the industrial application of materials due to wide application in various field such as oil refining, power plants, construction leading to utilisation of metallic materials such as iron and steel [7]. However, production downtime and replacement, as well as health and safety issues, are the resultant effects. In order to avoid these forms of depletion of metal at the earlier stages, the use of required materials, inhibitor and ideal preventive measures such as coating must be applied. Therefore, the negative environmental impact of corrosion has been a motivation over
the years for researchers to focus on the use of corrosion inhibitors from eco-friendly, biodegradable and renewable sources.

Over time, the existence of inorganic substances like phosphates, chromates, dichromates was reported as effective inhibitors against material degradation. In the dissolution of metals from their acidic or basic media, inhibitors are often added during industrial processes to combat corrosion of the mild steel [8]. Chromium (VI) as one of the carcinogen substances which is one of the heavy metals found in most synthetic inhibitors has been banned by World Health Organization (WHO) due to their toxicological effect on human and environment [5]. This action fosters the use of eco-friendly inhibitors as the best options to protect mild steel against corrosion using a green environment, which is renewable, inexpensive and sustainable corrosion inhibitors. There are reports on different chemical components from parts of plants, and relatively similar to that of conventional organic inhibitor molecules [5]. Corrosion prevention and inhibition are of a high operating expense in many countries around the world. A method to which corrosion can be rapidly eradicated or at least reduced will have to save cost each year. It is therefore very important to find new materials and methods that can be used to inhibit corrosion using eco-friendly corrosion inhibitors. Many studies have been carried out on the control of corrosion in aggressive media using plant extract [9].

2. Inherent Properties of Mild Steel

Mild steel, with carbon content in the range of 0.15 to 0.20%, universal form of steel and engineering material having relatively low price with excellent mechanical properties such as strength, ductility and malleability that are acceptable for various applications in several industries [10]. In most manufacturing industries like fertilisers and chemicals, oil refineries, nuclear power plants, among others, steel is used to make containers, steam generators, liquid-carrying pipes, and so on. Steels differ in their compositions, applications and classifications [9].

Classification of plain carbon steels, low alloy steels or high strength steels and stainless or chromium steels are classes of steels. Specific properties of alloy steels are improved by the addition of alloying element, improving the metallurgical properties and corrosion inhibition of low alloy steels which can be attained with the aid of copper to plain carbon steel. Steel surface coverage is enhanced by the protective coating of an organic-based primer. Generally, stainless steel with a minimum of 12% chromium and excess in nickel and molybdenum up to 6% are required to increase corrosion resistance. Molybdenum enhances pitting resistance and high-temperature strength forming a barrier of true oxide having a notable boundary between the metal and its surrounding environment [11].

2.1 Corrosion Reaction in Mild Steel

2.1.1 The Anodic and Cathodic Reactions

Corrosion processes occur at separate locations on the metal during oxidation and reduction process reaction. At the anodic site, the metal is a loss, giving rise to an oxidation reaction through dissolution, hydration or by complex formation. It serves as a major opening of a metal ion into solution. At the surface coverage and reaction stages, the formation of metal ion precipitates is noticeable. Metal oxidises to an ion carrying a charge with electron released, and then increases valence state as revealed in reaction:

\[ 2\text{Fe}^0 + 2\text{H}^+ \rightarrow 2\text{Fe}^{2+} + 4\text{H}^+ \]  \( \text{(aq)} \)  \[ \text{(aq)} \]

Anodic reaction:

Electrons are consumed at the cathodic surface due to electron released from the anodic reaction. Also, reduction reactions act at the cathode, unlike an anodic reaction where decrease in the valence state is a normal occurrence.

Cathodic reaction:
Overall reaction
\[
\text{Fe}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Fe(OH)}_2_{(s)} 
\]
\[(1.3)\]

Depletion formation produce by the oxidation reaction of Fe(OH)₃ (Rust)
\[
4\text{Fe(OH)}_2 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 
\]
\[(1.4)\]

(Lower, 2002).

2.2.1 Uniform Corrosion

Many instances of uniform corrosion have been placed as localised corrosion which involves non-stabilized coverage surface layer, the flow of velocity, a deposit of materials (siliceous substances) and metallurgical history [13]. A known structure of general corrosion can be mitigated using selected materials and application of corrosion inhibitor. Example of uniform corrosion is H₂SO₄ attack on the surfaces of zinc and iron, which is relatively detectable, resulting in depletion of metal surface on a tonnage yield basis. This could be prevented or controlled using proper materials, inhibitors, coatings and cathodic protection [12].

2.2.2 Pitting Corrosion

This form of corrosion exposes the degradation of the thin passive oxide film, part of a pit’s holes degradation type on a metal surface (aluminium and steels) in aggressive ions like Cl⁻, SO₄²⁻ present in the media. It is a hazardous form of corrosion, and its attack readily propagates and damages metallic surface quickly. This form is usually observed in oil and gas transmission pipelines [14].

Pitting corrosion acts as a chronic localised form of deterioration on a metal surface that led to pit formation on pipes surface. Pitting has a retention time before nucleation and growth, nucleation is off site-selective and microstructure dependent. For example, austenitic stainless steel is heated to temperatures, and the resulting alloy, the chromium-depleted site is subjected to pitting. Molybdenum serves as a more resistant alloy that gives a more protective and stable passive surface. The considerable check should be employed for materials that show pitting or has the tendencies to pit. This process involves three stages:

i. Adherence of surface coverage films on the steel.
ii. Initiation of pits at the localised region of vivid initiation.
iii. Continuous penetration of the material [15].

2.2.3 Cavitation and Erosion Corrosion

It is a unique form of erosion which enhances degradation, resulting in building up and collapsing bubbles inside liquid near the metal surface. This has been attributed to chemical and mechanical effects due to bubbles on the protective film, causing the newly exposed metal surface to corrode. The reformed film then gives rise to a new cavitation formation at the same spot. Cavitation corrosion can be prevented with the aid of using fluid pressure gradients and pressure drops limitation [9]. Alteration of environment, coating and cathodic protection are main preventive ways to combat these forms of corrosion [16]. Its appearance leads to
participating grooves, gullies, waves, rounded holes and valleys, which developed the surface film as resistance to corrosion. An example can be seen on a metal heater of a distiller with the aid of a protective scale formation of alkali corrosion product (slurries) and can be virtually seen on all types of equipment exposed to a moving fluid such as piping components like elbow, valves, blowers, heater and condenser. Selection of materials of better resistance to this form of corrosion inputs, designs, environmental changes, coatings and cathodic protection are ways to minimise damages or depletion due to erosion corrosion [17].

2.2.4 Stray Current Corrosion
Stray current corrosion occurs at the outward pipeline surface, which affects stray passage currents along the pathway of pipelines. It results in metal degradation in the form of localised or pinholes corrosion. The surface make-up of stray current corrosion behaves like a localised form of corrosion. Its corroding strength can be as a result of rapid perforation of pipelines. As for a foreign pipeline, it acts as a reverse current pathway for the cathodic protection system. In rare cases, rectifiers of cathodic protection are connected backwards in a way that direct current is discharged from the pipeline and anode of impressed current can be retrieved rather than discharging current [12].

2.2.5 Microbiologically-Influenced Corrosion (Mic)
This is the influence of microbial activities as it increases the rate of dissolution of metal. The microbial in this form of corrosion can be clarified using a classical and modern form of mechanisms. According to the classical mechanism, chemicals are produced from micro activities which are enhanced through an electrochemical reaction. The aids of sulfate-reducing, iron-reducing, iron-oxidising, and acid producing bacteria are the four main microbial species that accelerate the influence of MIC [17]. The stepwise reaction of sulfate-reducing bacteria requires the consumption of hydrogen atom to convert sulfate into sulfide, Sulfate-reducing bacteria activeness speed up the cathodic reaction and thereby increases the corrosion rate. During the anodic reaction, ferrous ion produced combine with sulfide ions to produce iron sulfide. Modern mechanism; mostly results in localised corrosion having the formation of a biofilm at the initial stage which comprises of several species of bacteria. Form of these activities reduces oxygen content within the biofilm, making the surface of the metal covered by biofilm to become anaerobic, having the solution as aerobic (saturated with oxygen). The biofilm creates a pathway area for bacteria to thrive and influence corrosion may be controlled by cleaving the surface to remove the biofilm or applying biocides to control the bacterial activity in the solution and increasing cathodic protection potential [18].

2.2.6 Galvanic Corrosion
Galvanic corrosion results in a severe attack to an underground structure such as pipelines in the oil field sector, resulting in intermixed activities. However, improvising a couple of new steel pipe alongside with an old steel pipe shows that the potential of bright new steel is typically negative to that of old rusted steel, which gives rise to the rapid corrosion degradation of the new steel. Also, this can be avoided if the new section of steel electrically insulated covering the old section of steel or cathodically protected. Selection and combination of metals that are closer in galvanic series insulate dissimilar metals where necessary. The different metallic surface has different corrosion potentials in a given media. Electrically-coupled metal that is cathodically polarised shows positive corrosion potential by decreasing its corrosion rate, where electrically-coupled metals of negative groups are anodically polarised with increased corrosion rate. Application of coating and addition of inhibitor products can combat this form of corrosion [18].

2.2.7 Crevice Corrosion
Crevice corrosion accelerates corrosion process formed between mating surfaces of metal assemblies, a localized form of corrosion embedded in crevice often start at the tail ends of
drill pipes joints, tubing collars or casting collars, leaving wide gap for liquid penetration through connector unit of pipe, and then making it too narrow for liquid to flow through [19]. Corrosion is formed uniformly over the entire areas of the metal substrates. As this depletion of metal continues in a crevice, depletion act invades oxygen leading to cathodic oxygen reduction end. Dissolution of metal ion progresses along with anodes within the crevice, resulting in an excess positive charge solution. Negatively charge anion ion like chloride moves to the enlisted anodic site [20].

2.2.8 Intergranular Corrosion
Difference in the concentration of impurities in the presence of galvanic elements is the major causes of this type of corrosion. Generally, metals solidify with unique forms of grains consisting of crystalline units. Moreover, the irregularity of the grains (a form of crystals on a microscopic scale that constitutes micro structure of metals and alloys), at the grain boundaries has resulted in the more susceptible dissolution of the metallic surface because of their reduction in mechanical properties and ductility of the substrates due to welding and stress cavitation. A classical example is the nitric acid test for stainless steels where more than 12% chromium is needed to make stainless steel, thereby increasing the corrosion resistance of chromium towards the grain-boundary areas. Weld decay act as a result of corrosion effect intergranular. Time and temperature effects provide one reason electric arc welding is used more than gas welding for stainless steels. The former produce higher and more intense heat within a short interval. The latter would keep metal in a broad zone sensitising range for a long duration, which means greater carbide precipitation. Employing high-temperature solution heat treatment, i.e. solution-quenching and rapid cooling, is viable solutions to prevent intergranular corrosion on austenitic stainless steel [18].

3. Corrosion and Categories of Corrosion Inhibitor
These are substances (chemical) that retard the corrosion process or possibly damage a given metal which is exposed to a specific environment. They reduce the overall corrosion rate of that site when added in sufficient low concentration in a media. Some accustomed benefits of using corrosion inhibitors are listed below:

i. Prevention of production downtime or shutdown.
ii. Prevention of accidents from brittle or structure failure.
iii. Prevention of heat transfer loss, e.g. in boilers, cooling plants etc.
iv. Preservation of attractive appearance.
v. Extension of equipment life span.
vi. Prevention of product contamination [21].

3.1 Inorganic inhibitor
Inorganic inhibitors drastically functions by passivating the metallic surface without the need for oxygen. Examples are nitrate and chromates ions, which can be reduced while they oxidise the metal surfaces to form a passive oxide film. Second generation phosphate pigments developed and incorporated elements such as aluminium, iron and molybdenum as a realistic alternative to chromates compounds in the formulation of protective paints usage. Commercially available pigments based on calcium-exchange silica gel are incorporated into polyester primer and show effectiveness as a cathodic inhibitor [22].

3.2 Organic inhibitors
[23] Reported that organic inhibitors might serve as an oxide film coverage to the surface of an anodic and cathodic, which frequently prevent depletion of metal substrates as predominant film-forming surface adsorption. The strong affinity for metal surface compounds can be evaluated through the inhibition potential of an organic inhibitor products. Protective hydrophobic film molecules are built up mainly on the metal surface which inhibits corrosion via the dissolution of metal in the electrolyte. Organic inhibitor molecules are interfaced with
four primary modes of adsorptions namely; corrosion inhibitor (CI) forming an electrostatic
interaction with the metal substrate (physisorption), charge movements between the metal
surface and CI (chemisorption), π-bonding, and organometallic complex formation. For
organic compound films/layers to adhere on the metal surface, the nature of the functional
group, aromaticity, possible steric hindrance, electronic density of donors, corrosive medium
and nature of the interaction between the p-orbital with the d-orbital of iron must be ascertained
[24]. Organic amines are majorly the most important constituent class of organic corrosion
inhibitors. In acidic condition, organic amines acidic components form an amine salt which
then coats the metal, thereby preventing further corrosion. Newer and greener inhibitor have
resulted in the reduction and usage of many toxic amine compounds or salt, giving rise to the
introduction of new, less toxic, organic amine compounds or salts as replacements. An example
of these changes is the use of aliphatic amine instead of aromatic amines of a green inhibitor
[23].

3.3 Green corrosion inhibitor
Promising future of “green” inhibitors has shown a landmark of good quality in the
environment due to the lack of toxic compounds like heavy metals. They are a biodegradable
and renewable source of materials [25]. Plant products have natural organic constituents like
tannins, alkaloids and pigments that exhibit inhibitive actions. Moreover, a simple process or
method of extraction is at a low cost. Green products are produced following a set of principles
designed to kick against the use of hazardous chemical substances in the industry for an
enabling safety and sanitation of the environment. Green inhibitors have been the most
anticipated eco-friendly and low-cost products worldwide. Plants composed of natural organic
compounds like tannins with complex structures and numerous heteroatoms are of established
inhibitive properties. The inhibition effects of the tannins, alkaloid (berberine for the metal in
acidic media) had been demonstrated using theoretical and experimental methods [25]. Pectin
has been studied as an effective green environmental friendly inhibitor for corrosion studies of
aluminium in hydrochloric acid [26]. Moreover, polymeric extracts of leaves and seeds are
being employed as effective inhibitors for metals and alloys in several common electrolytic
media [26].

3.4 Applications of Corrosion Inhibitor
Inhibitors used in coatings are exposed to open atmosphere environment. Moisture comes in
contact with paint, thereby leaching out some inhibitory fluids to protect the metal. A
moderately dissolve substance of an inhibitor can adequately leach out insufficient amounts of
fluid in protecting the metal with a long-term approach, but not so soluble that it will be lost in
the short term. Common usage of most coating inhibitor over the years and in recent times has
led to a high range of toxicity and adverse health effect. Lead compounds are bio-accumulative,
ingestion, inhalation or skin absorption of red lead can result in skin disorder. Also, the
hexavalent chrome in zinc chromate pigments is a known carcinogenic substance which is
likely to cause skin sensitisation and reproductive disorders. Due to all these adverse health
effects, their findings work to focus on the development of new environmental-friendly and
non-toxic anti-corrosive pigments. Many new substituted pigments such as zinc phosphate,
calcium phosphate, aluminium phosphate, barium metaborate and some synergistic
compositions have been widely studied to determine their performance as primers against lead
and zinc chromate primer [27].

3.4.1 Continuous Injection
This form is mostly applicable in systems where the distributive act cannot be achieved evenly
and moderately through the inlet passage of fluid. Its application can be found or acknowledged
for water treatment plants, cooling water for turbines in power plants, gas wells, gas lift wells,
with the of injection pump or dosing pump whereby the fluid inhibitor is injected. Most chemical injection pumps are quite reliable and require little servicing or diagnosis, regulated to deliver at its programmed rate. Boilers, portable water production and recirculating fluid system also followed this form of system application [27].

3.4.2 Batch Treatment
Batch treatment is mostly applied in an automobile cooling system where a known quantity of inhibitor is added at one time throughout the entire surface coverage for a lengthened space of time, from the top with an existing one. Perhaps, the old solution which might drain, replace and refill with a stock solution. Relating to the aeration, the close-loop cooling system requires constant checking of the inhibitor product concentrations to maintain standard operating range limits. This approach found its application in treating oil and gas wells, such that the inhibitor products are made up with an appropriate solvent, and with the aid of dosing pump which is programmed to dose into the gas well of open-hole that have a packer [27].

3.4.3 Precipitation inhibitor
These are film-forming compounds with the notable formation on the metal surface which interfere with anode and cathodes indirectly. Silicates and phosphates are the most commonly readily available class of this inhibitor. For cooling water system having a pH of 7.0, low concentration of chloride, silicates and phosphates caused by passivation of steels when oxygen is present, they behave as anodic type inhibitors. Deduced setback of silicate and phosphates are relatively dependent on water composition [28].

4 CHEMICAL FACTORS AFFECTING CORROSION
4.1 Dissolved Oxygen (DO)
[14] captured the effect of Dissolve oxygen (DO) on metal substrate which brings about degradation of protective hydrogen film that oxidises dissolved ions into insoluble form (metal precipitates).he also deduce that parts of dissolved gases (oxygen, nitrogen, carbon dioxide, ammonium, sulfurous gases) which support aquatic life are also responsible for corrosiveness of such water towards metal and volumetric ratio of oxygen in water which aids photosynthesis. He reported that this challenge could be prevented or minimised by mechanical action and chemically scavenging the remainder. The mechanical approach makes use of vacuum degasifiers to reduce the oxygen level to less than 0.5-1.0 mg/L or de-aerating heater to reduce oxygen concentration to the range of 0.005-0.010 mg/L. Chemically approach involves the use of hydrazine and sulfite. Using sodium sulfite as an effective scavenger has a confined system operating limit about 1000 psi forming corrosive hydrogen sulphide and sulphur dioxide shutdown occurrence. Hydrazine is more efficient to eliminate the residual oxygen by reacting with oxygen to give water and gaseous nitrogen, which are quite recognised as a toxic substance.

4.2 Chloride Ions
[14], also evaluated the effect of some chemical substances such as Sodium salts (chloride, sulfates, nitrate, bicarbonate, salts of heavy metal, silica etc., which are part of mineral constituents occurs in the presence of chloride ion at a temperature over 300 F (180 °C), forms a unique type of corrosion, which can grow under porous iron sulphide deposits. The acidic form of iron (II) chloride from chloride ion, which prevents iron sulphide layer on the corroding steels enables the anodic reaction to continues having hydrogen as products which are known as hydrogen embrittlement. It was ascertained that the corrosive nature of carbon dioxide act as a function of forming hydrogen ion. When carbon dioxide dissolves in water, its effects lower the pH and increases the corrosion rate. Relatively, oxygen as predominant corrosive gas
in the oil field sector, has a severe corrosive effect at a concentration 50 ppb alongside with any other acid gases.

4.3 Effect of Flow on Corrosion
[11], reveals that pressure drop, flow regions and locations are sites where corrosion may take place (i.e. where water accumulates). The effect of flow can be viewed in three different directions; mass transfer, momentum transfer, and phase transfer. The mass transfer involves the flow of corrosive species like dissolve oxygen towards the metal surface or washing away of corrosion product on the metal surface. He deduces that the flow rate may decrease the corrosion rate by removing corrosive species from the metal surface. Moreover, also, momentum transfer is a form of flow-induced localised corrosion which is affected by turbulence intensity and mass transfer, phase transfer; its flow may affect corrosion in parts leading to erosion and under deposit corrosion.

4.4 Effect of Temperature
Generally, the corrosion rate accelerates with increasing temperature up to a maximum point. According to [11], it is difficult to establish the formation of a FeCO$_3$ surface layer at a temperature below 70 °F (20 °C). For a temperature range of 70 and 100 °C (20 °C and 40 °C), the surface layer formed is not adherent enough and can easily be wiped off using cloth. Also, in the range between 100 and 140 °F (40 °C and 60 °C) are non-protective. Lastly, these range of temperature between 140 and 300 °F (60 °C and 150 °C) are investigated to be hard, adherent and protective. The negative aspect of temperature change reveals that at 70 °F (20 °C) are the non-uniform, fragile surface layer. Pitting corrosion are mostly subjected to this form of effects. As both the pit density and pit depth decreases, the temperature increases, leading to the formation of adherent and protective surface layer on the substrates.

4.5 Effects of CO$_2$
Several investigations and reports have been made to study the degradation of plain carbon steel in CO$_2$ media. CO$_2$ are quite soluble substance in the aqueous phase, having its concentration been increased with decrease in apparent temperature ranges for CO$_2$ solution concentration are 265-320 ppm at 80 °C (176 °F) at 1125-1720 °C at 20 °C (68 °F). The dissolution of CO$_2$ in water forms a hydrate to become carbonic acid (H$_2$CO$_3$).

Thus, the overall corrosion of low carbon steel in a CO$_2$ environment is given as:

$$\text{Fe} + \text{H}_2\text{CO}_3 \rightarrow \text{FeCO}_3 + \text{H}_2$$

Approaching solubility level, concentrations of Fe$^{2+}$ and CO$_3^{2-}$ give room for corrosion degradation without a corrosion layer and vice versa. An intact FeCO$_3$ surface layer can prevent corrosion. When FeCO$_3$ was broken, localised and pitting form of corrosion occurred [11].

4.6 Effect of Pollutants
[29], reported the significance of pollutant during refining operation, especially combustion of fuel, a derived sulphur containing products such like coal, diesel, gasoline, and natural gas, where SO$_2$ had been identified to be of gaseous substance and as one of the air pollutant that affects depletion of metal surface. Another product of combustion corrosion. When FeCO$_3$ was broken, a localised and pitting form of corrosion occurs.

5. Conclusions
Corrosion of metals is confronted with several challenges such as decrease in yield, ductility, and ultimate strength, failure of operating equipment, bridges and constructions. in order words, This foster scientific recognition to develop more effective, environmental friendly or natural product corrosion inhibitors also called “green inhibitor” due to its availability, renewable, inexpensive and ecological source of material so as to serve as a constructive
organic phenomenon that prevent or combat depletion metal surface which is widely used in the oil and gas industry and has proven to be very successful. This has led to use of eco-friendly inhibitors as best options to protect a substrates against corrosion for an achievable green environment.

Acknowledgement
The author appreciates the department of Chemistry, Covenant University, Ota for the support offered to carry out this research work.

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