Chemistry International 6(4) (2020) 232-259

International Scientific Organization
http://iscientific.org/
Chemistry International
www.bosaljournals.com/chemint/

Green and eco-benign corrosion inhibition agents: Alternatives and options to chemical based toxic corrosion inhibitors

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ARTICLE INFO

Article type:
Research article
Article history:
Received November 2019
Accepted March 2020
October 2020 Issue
Keywords:
Corrosion inhibitor
Green alternatives
Plant extracts
Halides-surfactants
Extraction method

ABSTRACT

The control of corrosion of metal and its alloy dissolution in environments that induce corrosion has been reviewed showing successes recorded in the search for alternative inhibitors that would replace toxic and expensive inhibitors that in some instances require rigorous process of synthesis. Studies show that organic compounds, drugs, polymers and extracts from plant have been used. It also shows that in an effort to improve the efficiency of the developed inhibitors quite a number of them have been synergized with halide ions and surfactants. The mode of adsorption mechanism for majority of the tested inhibitor alternatives is also highlighted.

Capsule Summary: A review of corrosion inhibitors derived from organic compounds, drugs, dyes, polymers and extracts from plants and the synergy of these type of inhibitors with halides indicating the possibility of blending crude plant extracts with polymers to inhibit corrosion efficiently.

Cite This Article As: V. O. Izionworu, C. P. Ukpaka and E. E. Oguzie. Green and eco-benign corrosion inhibition agents: An alternatives and options to chemical based toxic corrosion inhibitors. Chemistry International 6(4) (2020) 232-259. https://doi.org/10.5281/zenodo.3706592

INTRODUCTION

Corrosion has been a challenge to metals such as mild steel and carbon steel that is widely used in many applications such as construction, petroleum production and refining, chemical processing, marine applications and construction. (Fouda et al., 2005; Fouda et al., 2017; Ramesh et al., 2001). The Oil and Gas industry stands out as a business concern that has extensive capital investment in assets such as offshore facilities, drilling rigs of different kinds, upstream facilities, pipelines for hydrocarbons both liquid and gas and terminals for discharge. The list of assets also includes facilities in the midstream such as refineries and downstream segments assets such as farm tanks and trucks. These multifaceted plants, properties and equipment are enormous and call massive capital investments to own them and when they corrode they become waste with minimal composition at any dump site although with some level of reusable property (Izionworu and Akpa, 2014). A study conducted a couple of years ago on some of the upstream oil and gas companies such as BP, Shell Petroleum Development Company, Conoco Phillips, Exxon Mobil, and TOTAL E & P) demonstrate that capital investment on plants, properties, and equipment accounts a little above average of the total assets valued $100 billion (Nicholson et al., 2010; Ossai, 2012). A major component of this massive infrastructure is metal – mild steel, carbon steel, aluminium etc, of different grades and metal because of its nature and tendency to return to a natural state comes under attack by corrosion in different environments and media. Yes, corrosion tend to undermine this huge investments resulting in loss of resources. While this menace rages on globally, Nigeria has had its fair share of the troubles of corrosion.

In Nigeria, the cost of corrosion to metal assets in all industries is quite alarming particularly in the oil and gas industry. In 2012 with reference to an onshore production facility data Oil Mining Lease (OML) 24, which is located in South-Eastern Nigeria, Akinyemi et al., (2012) observed that the cost of corrosion associated with the activities of that plant for by just one company alone was higher $2.5 spread across five years 2004 to 2008.

The cost implication of corrosion at global level is nothing different from that locally in Nigeria. With the continuous growth in the oil and gas industry massive capital expenditure continues. Also, in response to the global need for fossil oil there has been improvement in technology and the technique to explore oil and gas in both onshore and offshore facilities (Ossai, 2012; Report on Oil and Gas Enhanced Production Services Industry, 2016). The increase in demand has also come with so much pressure on all facilities which in turn increase the cost of maintenance which has hit all time high mark. (Nicholson et al., 2010; Ossai, 2012). A research conducted ten years ago reveal that Europe's average major containment hazards recorded from 180 to 2006 were all associated with technical failures of plant facilities (Horrocks et al., 2010). These failures are expanded to include aging, erosion and fatigue. Indeed, it can rightly be said that the western world has had its fair share of the devastating effect of corrosion.

The United States have been badly hit by corrosion in recent years. In a research by Ossai (2012), he referenced the report by Health Safety and Executive (HSE) Offshore Technology Report (2012) on the Review of Corrosion Management for Offshore Oil and Gas (O & G) processing. As seen in that report the US had a record 1$ trillion spent on managing corrosion associated costs. This is considered disturbing because the 6.2% of US Gross Domestic Product (GDP) was used to manage corrosion as reported it is a the only single expense with the largest chunk of expense in the American economy. This whooping cost corrosion control related and corrosion accounts for a quarter of 100% of all assets failure and this cost cuts across all production stages in the oil and gas industry in this country. Also, drilling mud have been found to corrode well pipeline, drilling equipment, casing and the environment. All of these add up to the cost of managing corrosion (Guo et al., 2020; Han et al., 2020; Ogunleye et al., 2020; Ser et al., 2020).

Also, with the progress made in deep water (or deep sea) O & G exploration the eventual expense for corrosion continues to soar. National Association of Corrosion Engineers (NACE) recently put the annual cost of corrosion at a whooping estimate of $1.372 billion (NACE, 2016). When broken down this figure shows that $589 million was spent managing pipeline surfaces and facility. $463 and $320 million were spent annually managing corrosion related to downhole tubing and capex associated with corrosion control respectively. The 2016 NACE report also puts the cost of corrosion mitigation at US$2.5 trillion. This figure is about 3.4 percent of the world's GDP. This staggering cost is calculated based on the estimate that about 5000 kilograms of steel degenerate per second all over the world, 40% of all steel produce are used as replacement parts for parts of assets that have been corroded while 60% of the offshore fleet all over the world have been used beyond their estimated 20 years' design age. Another 6 tons of 60% offshore fleets are platforms that are stationary (Mark et al., 2014). The NACE report under review heightens the concern with the disturbing figure of about 60% corrosion control and maintenance cost directly spent on offshore facilities maintenance and that spent on managing coating failures. The later cost is between 15-20 times more expensive than cost incurred from new construction activities in a company yard (Gerhardus et al., 2016; Global Market Research, 2012).

Corrosion is indeed a menace that needs to be controlled at minimal cost to increase return on investments. An efficient cost effective control will partly depend on a deep understanding of the causes of corrosion and a number of agents have been identified as corrosion causative agent (Akinbulumo et al., 2020; Aquino-Torres et al., 2020; Chaouiki et al., 2020; Wang et al., 2020). The list includes the most material in the universe, water, acid and CO_2. Water comes to play during transport of crude in the pipeline and this causes corrosion. The Formation water that comes with the product during drilling also cause corrosion. The acid used in pickling action on well tubing or scale removal cause corrosion while the produce CO_2 and CO_2 injected for secondary recovery also have very serious negative effect on the completion strings (Brondel et al., 1994). So, pipelines come under attacked by CO_2 and H_2O. They also attacked by bacteria in the case of Microbial induced corrosion (MIC). There is also the sand and H_2S influence. Other fixed mechanical support equipment in the O & G industry comes under attack as well. They include separators, valves, vessels tanks, and more are vulnerable to different kinds of corrosion, however an efficient cost effective corrosion control would include the option of optimization and reliability checks (Dehghani et al., 2020; Farahati et al., 2020; Kamali Ardakani et al., 2020; Lgaz et al., 2020; Neelamkavil, 2009; Solomon et al., 2020).

A reliable reliability check will focus on corrosion control cost reduction in all O & G assets (Nicholson et al., 2010; Ossai, 2012). Industry operatives are giving attention to an initial plan of facility that includes a corrosion management plan for all phases of production in the entire facility. To achieve the overall aim collated data from existing oil and gas plants are integrated into design parameters for new facilities such that necessary and adequate corrosion management methods geared towards enhancement of the design life of oil well assets – tools, equipment, accessories to meet production objective at minimal cost is achieved (Khajota et al., 2007; Raju, 2009). In addition to efficient asset management, many asset owners have used different methods of corrosion control amongst which is corrosion control through use of protective coats such as painting of metal, electroplating and use of grease and oil in the least. Some have employed use of hydraulic systems that reduce the velocity of the fluid in use, oxygen removal using oxygen scavengers, and deliberate effort towards reduction of the pH of the working fluid and use of inhibitors. Oil field operations seem to require and fancy film forming inhibitors composed primarily of inorganic oxygen, H_2S scavengers, oxidizing agents, surfactants (Umoren and Solomon, 2014). On the other hand, a variety of organic inhibitors such as acetylenic alcohols, amines, imidazoline, iminium salts (Finsgar and Jackson, 2014) have also been used. These options are not without their various challenges.

The existing challenge

The use of different forms of inorganic and organic inhibitors such as Volatile inhibitors, Passivating inhibitors, Film inhibitors and Cathodic inhibitors has been welcomed in the past, particularly in the oil and gas field operations where they have yielded positive results in terms of reduced failure of installations and hence increased revenue. However, despite the successes recorded by the use of inorganic and organic inhibitors in corrosion control in all applications of metal and particularly during acid pickling action on well tubing, acidizing process, tank descaling and industrial cleaning, there are issues around their suitability and health implications (Finsgar and Jackson, 2014). As an example, it has been reported (Umoren and Solomon, 2014) that chromium compounds used in corrosion control of metals in aqueous environments exhibit high level of toxicity leading to its usage being banned in any industry. Another inhibitor, lanthanide salts have been used until it was reported to have the same toxic effect as lanthanide chlorides. Vapor phase corrosion inhibitors have also been reported to be toxic and carcinogenic in nature (Subramanian et al., 2000). Again, although synthesized organic inhibitors have proved useful in terms of their ability to dissolve completely in aqueous environment that is corrosive, their ability to easily get attracted to metal surfaces and the stability associated with them when they are adsorbed on metal surface, the high cost of synthesizing them is a serious challenge as well.

The environmental, health and economic challenges gave rise to the increasing search for cheap, convenient, safe and environmentally friendly corrosion inhibitors (Umoren and Solomon, 2014) from natural organic substances that are usually biodegradable in nature to be used as corrosion inhibitors. Reports on different plant extract inhbitors abound and the list includes low-grade leaves of plants, honey, gram flour, onion, roots of plants, shells of plant fruits, potato, gelatin, flowers, plant seeds and gums. These various insect and plants products have been reported in different research reports as suitable inhibitors. Several research work have tested these alternative sources of corrosion inhibitor on carbon steel, mild steel and nickel sheets, while other studies have been performed on aluminum sheets (Amitha and Basu, 2011). Many other researchers have delved into sourcing for polymer based inhibitors as replacement for the toxic and expensive inorganic and organic metal corrosion inhibitors (Umoren and Solomon, 2014).

Not much investigation has been done on blending efficacy of plant extracts and polymers. It will therefore be of interest to replace develop or design of inhibitors from a blend of polymer and plant extract to provide inhibitors that are cheap, environmentally friendly, safe for human handling and biodegradable to replace toxic inhibitors that cause harm to humans and the environment.

General overview

Metals or alloys corrosion can be defined as the gradual degeneration of the structures to their stable form commonly referred to as oxides. This destructive attack takes place when metals or alloys are exposed to environments that set up the process or instigate it. The process is usually not reversible and happens on the exterior of the metal in an electrochemical reaction that involves two half-reactions going on simultaneous: the metal coupon oxidation and the oxidant reduction (Mu et al., 2005; Oguzie, 2004).

i) The process of anodic reaction

$$Fe^{2+} + 2e^{-} \rightarrow Fe \qquad (1)$$

ii) The process of cathodic reaction

Reaction in acidic media

$$2H^{+}_{(aq)} + 2e \rightarrow H_{2(g)} \qquad (2a)$$

Reaction in neutral/alkaline media

$$O_2 + 2H_2O + 4e^{-} \rightarrow 2OH^{-} \qquad (2b)$$

As established by Christov and Popova (2004) the above are simple corrosion reaction taking place at different sites on the metal surface simultaneously. They are referred to as half-cell reactions of anodic and cathodic nature. The main reason for this reaction is that metals are more stable with a tendency to return to their original state of existence as ore. This state is achieved as the metal reacts with oxygen and water in the environment the metal is found. Also this reversal is driven by the nature of most metals to achieve a state of lower energy by forming the metal compound. More metals exist in this state of natural preference. Since corrosion processes are naturally electrochemical, iron atoms are oxidized to ions and release electrons that avert anodic reaction. This dissolution continues in this order where the electrons that have been released are able to locate another cathodic site where it can settle and continue the cathodic reaction. This mobile electron in a cathodic environment will leave the metal surface if it reacts with components of the electrolyte that can be reduced. Based on Faraday's law, the reactions in the anodic and cathodic sites of a metal must be equivalent in rate and will be determined by the total "corrosion current" (I_{corr}) density that flows as electrons from the anodic to cathodic region. The flow of I_{corr} which is essentially by ionic conduction in the electrolyte coupled with the conductivity of the electrolyte will determine the corrosion behavior. (Wang et al., 2011).

Types of corrosion

Alloys and metals are prone to corrosive deterioration and this takes different forms which include Oxidation corrosion, Concentration cell corrosion, Galvanic corrosion, Pitting corrosion, Crevice corrosion, Uniform corrosion, Erosion corrosion, Intergranular corrosion and Microbial influenced corrosion.

Oxidation corrosion

Oxidation corrosion is one form of corrosion that is very common. In this type of corrosion, there is a combination of metal atoms and the atoms of oxygen leading to formation of the metal oxide. The reaction leaves notable evidence commonly seen as Iron rust. Virtually all metals and alloys are disposed to revert to their original state. The other different types of corrosion are briefly explained below:

Uniform corrosion

In this form of corrosion, the corrosion attack occurs on all parts of metal shrinking all of its part until the metal fails. Uniform corrosion usually occurs when a chemical attacks an exposed surface of a metal a typical example is an acid attack on a metal. It is a direct type of attack. The mode of operation of this attack is etching of the metal. For polished surfaces the chemical attack will result in the metal surface becoming dull, proceeds to become rough is the attack is sustained and then the surface gets damaged as more grave corrosion may begin. This type of corrosion presents little engineering challenge since exposed structures will normally be treated with corrosion control measure before a major defect arises.

Galvanic corrosion

Galvanic corrosion occurs when two metals in an electrical circuit are immersed in an electrolyte A common occurrence of this type of corrosion is on structures that are used for construction or any other purpose in a sea water environment. Scenarios like this result in the setting up of what is referred to as galvanic couple. In this situation, a component of this couple, plays the role of the anode and other part of the metal component serves as the cathode with lesser corrosion taking place in that region. The science behind this type of corrosion over time formed the basic root of most corrosion investigation and observation modus operandi. Again, the use of the principle of this type of corrosion or coupling has been employed in the protection of metals.

Concentration cell corrosion

This is a type of corrosion that occurs when diverse a portion of a piece of metal or a metallic member is exposed to different concentrations of a corrosive media. Diverse parts of the surface of a metal come in contact with varying concentrations of a particular solution. This type of corrosion exists in three different forms namely:

i. cells with concentration of metal ion
ii. Cells with Varied Concentrations of oxygen and
iii. Active-passive cells.

i) ***Cells with concentration of metal ion:*** In this type of concentration cell based corrosion high concentration of metal ions clog up under faying surfaces, that is surfaces that are connected by either bolting, use of rivets, soldered, welded or joined using adhesive, in the presence of water. Areas of lesser concentration of metal ions grows at locations close to cracks created by the faying surfaces. When the above condition exists the part of the metal that has lesser metal ions concentration becomes the cathodic reaction site and the part with more metal ion concentration acts as the anode with much more corrosion taking place there. So the cathodic part becomes protected from the ravages of corrosion. The corrosion is quite fast at the anodic site. The situation is prevented by ensuring that all faying surfaces are well coated preventing moisture that creates opportunity for the initial metal ion build up.

ii) ***Cells with varied concentrations of oxygen:*** This type of corrosion cell develops when oxygen dissolved in a solution of water on a metal surface is not evenly distributed by diffusion. If the concentration of the oxygen is more on any part of the surface a difference in oxygen concentration sets in creating cells of that status. In the event of this situation the part of the metal with the lower oxygen concentration experiences more corrosion. This is common with metal surfaces that are around gaskets, rubber, wood, plastic or any other material that is not metal. The area of lesser oxygen concentration becomes the anode and allows corrosion to thrive. Notice that there no metal deposits but speaks of dusts, debris or dirt's. Faying surfaces create opportunity for this type of corrosion. To prevent this type of corrosion sealing or coating can be used.

iii) ***Active-passive cells:*** Active-passive cells are corrosion causing sites that develop in all metals that require passive film for protection of their surfaces. A typical case in point is the austenite metal, a steel material that resists corrosion. The situation occurs when first oxygen cell corrosion occurs. This happens when water containing salt drops on the metal surface and the water contains oxygen which forms an oxygen cell because it has higher concentration of oxygen. When the later happens and then the film cracks opening up and exposing the metal surface. That exposed metal surface becomes the anode and the rest of the metal still under coat becomes the cathode and corrosion does not happen there while the anode part, that is the exposed metal surface begins to corrode because of the active-passive cell that has developed. This type of corrosion is controlled by continuous metal surface cleaning and coating as the need may be.

Pitting corrosion

Another form of corrosion is the pitting corrosion. This type of corrosion is another form of localized corrosion where confined holes or cavities exist on a metal material. This type of corrosion is presents detection and prediction and manage when compared with uniform form of corrosion because it can be concealed by products of corrosion. Getting the right kind of engineering solution to this form of corrosion can be very difficult as a result of this. Pitting corrosion, is a common localized corrosion that attacks a metal behind the seen as it were. The shape can differ from hemispherical to cup-shaped that is closed with semi-permeable membrane or opened to the atmosphere. Pitting occurs via any of the following:

a) Disintegration or total breakdown of protective oxide film as a result of Localized chemical or mechanical interaction that goes on in the presence of low oxygen concentration and it attendant effect on the oxide film, factors that affect water chemistry and high concentrations of chloride as in sea water).
b) Specific destruction of protective coats and or wrong application of the coats.
c) Lack of a uniform metal structure and surface likely because of a combination of both metal
and non-metal structures as components in industry installation.

Crevice corrosion

Crevice corrosion is a type of localized corrosion normally originated by chemistry inside the vicinity of the crevice. This occurs when a very small solution settles under gaskets, fastener heads, washers, lap joints, disbanded coatings, and then the situations progresses when the following conditions exist:

i) Inhibitor depletes or loses its concentration
ii) Oxygen level depletes in the crevice
iii) Emergence of acidic conditions due to shift in pH level and
iv) Upsurge in the number of aggressive ion species present in the crevice.

Intergranular corrosion

Metals and alloys consist of grains and boundaries of the individual grains that separate one grain from another. Intergranular corrosion is a form of corrosion that is localized along the grain borders of a metals and alloys or positions adjacent to it. When a section is affected that part alone is affected the other part of the grain may remain unaffected. This corrosion type result from chemical exclusion that results into the loss of important elements that can possibly reduce corrosion, when this happens and grows overtime as more impurities add up leading to increase the chances of corrosion due to phases that are triggered to surface, corrosion sets in and can eventually affect the entire grain boundary line causing disintegration of the metal. As always the weaker section of the grain boundary becomes the anodic site while the unaffected parts of the metal is the cathodic site.

Erosion corrosion

Corrosion due to erosion occurs when a corrosive fluid is in motion relative to metal surface that is stationary. If pitting corrosion has occurred already the fluid in motion will increase the rate of corrosion. This is especially so in internal surfaces of tubes. The situation becomes worse with faults resulting from errors caused by workmen who create burrs at the end of in the tubes when tubes are cut instead of buffing them. Usually a high rate of pitting is observed when erosion and corrosion process are combined, a typical case in point is the industrial processes where machine or assets interact with sand-bearing liquids.

Corrosion caused by microbial

This kind of corrosion is referred to as microbial influenced corrosion. it is initiated by microorganisms, that produce acids as by products. The microorganisms produce acid through their metallic routes resulting into corrosion of the base metals.

The mechanism of iron corrosion

Mild steel has been used for different industrial purposes and their use is born out of their availability, less fabrication challenges cheap with good mechanical properties. Because it is readily available it is commonly used with high potential for corrosion taking place. One major challenge is corrosion caused by acid attack. The situation is common when cleaning is done, during transportation of chemicals like acids etc. The actual mechanism of iron and steel corrosion is very complex as it delves into the chemistry and electro-chemistry and Iron will corrode only in the company of both H_2O and O, forming an Iron oxide. This corrosion as established takes place as two separate reactions in an acidic environment, that is anodic and cathodic reactions. The anodic reaction in acid corrodent solution leads to Iron dissolution which has been reported to proceed according to the mechanism below.

$Fe + OH^{-} \rightarrow Fe\,OH_{ads} + H + e$ (3)
$Fe\,OH_{ads} \rightarrow Fe\,OH^{+} + e$ (4)
$Fe\,OH + H^{+} \rightarrow Fe^{2+} + H_2O$ (5)

As a consequence of these reactions, there is weight depreciation since the products of iron corrosion are very soluble, they get dissolved in the solution the iron is immersed in. In acid solutions without restraint, electrons react with hydrogen ions form hydrogen gas in the corrodent that get attached to the metal surface (Oguzie, 2007). This reaction is the cathode reaction.

$2H^{+}_{ads} + 2e- \rightarrow H_2\,(g)$ (6)

For steel in contact with water, the cathodic reaction proceeds as seen below:

$O_2 + 2H_2O + 4e- \rightarrow 4OH-$ (7)

Corrosion process determinant factors

A good number of factors upset corrosion progression and they comprise of: the metal type involved, quantity of oxygen dissolved in corrodent, concentration of corrodent used, environmental condition, temperature, corrodent concentration, pH, electrode potential, and nature of corrosion products.

Corrosion control

Corrosion control can be realized through any of the ensuing ways: Isolation of metal from corrosive media, use of corrosion inhibitors

Metal isolation

Isolation of metals from causative agents of corrosion is one sure means of ensuring that corrosion resulting from electrochemical reaction is control is using inhibitors. Among the different methods available for prevention of corrosion in fluid environment include use of barrier coating using polymers (Zarras et al., 2003). Polymer resins such as polyester, epoxy and acrylic thermosets commonly used in polymer concretes as stated by Izionworu and Dagde (2014) have also been used to coat metals during experiment as it is in electrochemical investigations. Another form of isolation is the application of corrosion retarders that are referred to as inhibitors. It has been a practice in various industries to use inhibitors which come in different forms. Ali and Foaud (2012) has reported on this, along with Bouklah et al. (2006), Ashassi-Sorkhabi et al. (2006) and Oguzie (2005).

Use of corrosion inhibitors (retarders)

Corrosion retarders are additives that are used in minor quantity in aggressive environment to prevent, reduce corrosion of a metal in that environment. These additives known as inhibitors act by adsorbing on the exterior part of metals exposed to corrodent situation. Their action on the metal surface also follows any of the following. In some cases, more than one of the below takes place (Amitha and Basu, 2011):

i) Retarder ions/molecules attachment on the exterior of metal undergoing attack.
ii) Accumulation or diminishing the acidic, the anode/or cathodic reaction.
iii) Reducing the speed at which reactants diffusion to the exterior of the metal.
iv) Reducing the resistivity of metal surface to flow of electrical current.

In recent times researchers have directed their attention to discovering natural inhibitors that are cheap and less expensive. Their interest has been on identifying natural molecules that can easily get adsorbed on metal surfaces. Plant extracts have been identified to have organic compounds like Ascorbic acid, Phytic acid, etc. these compounds act by getting attached on the exterior of the metal. In research published in 2007 Oguzie demonstrated this as was done by Amin et al. (2007) also, and other researchers (Abd-El-Nabey et al., 2006; Bouyanzer, Hammouti and Majidi, 2006; Chauhan and Gunasekaran, 2004; Raja and Sethuraman, 2008a and 2008b) also established this. These corrosion inhibitor according to Umoren and Solomon (2014) can be grouped as follow:

i) Organic
ii) Film
iii) Cathodic
iv) Volatile and
v) Anodic (Passivating) inhibitors

A brief discussion of each of these classes is presented in this review in no particular order

i) Cathodic inhibitors: This type of inhibitors reduces corrosion of metal by preventing cathodic reaction from taking place. Usually oxygen is produced at the cathodic site for environment that is neutral while there is hydrogen evolution on acidic environment. So, the cathodic inhibitor would form species that precipitate on the cathodic region reducing or lowering the reaction and diffusion going on at the site. Inhibitors of this type work in three ways:

a) Oxygen scavenger: The role of the oxygen scavenger is to forage on any oxygen present in the system, this actions presents cell concentration from developing leading to corrosion. This removal of oxygen is usually by oxygen scavengers present in the compounds contained in the organic inhibitor. A product is formed when the oxygen scavengers react with any oxygen in the system.

b) Cathodic precipitate: Here compounds like calcium and magnesium precipitate as oxides on exterior the metal. The precipitates remain and act as a shielding film separating the exterior of metal from the attacking acid ions.

c) Cathodic poisons: The use of cathodic poisons suppress cathodic reduction process by preventing any possible recombination of hydrogen and its discharge. However, there is challenge with this process as the hydrogen produced may cause cracking of the metal if they do not form hydrogen atom which makes them incompetent to cause any further harm to the metal if they get adsorbed again on the corrosion active site. Examples of cathodic poisons are Arsenic and Antimony are good examples of this type of inhibitor

ii) Volatile inhibitors: This type can be referred to as vapour phase inhibitors (VPI) or retarders. VPI's are retarders that acts in vapour form because they occur in vapour form and are also volatile in nature. This type of inhibitors has been found to be useful in preventing corrosion of metals exposed to vapour. To prevent corrosion of metals exposed in this type of situation, VPI molecules diffuse to the exterior of metals and gets attached on the metal exterior and are hydrolyzed leading to release of protective ions by the inhibitor. These include species like nitriles, aromatic, amines such as cyclohexylamines, aminonitrobenzoates, aliphatic etc. for inhibition of ferrous and nonferrous metal, (Subramanian et al., 2000). The applicability of these type of inhibitors has been found effective where grease, oil etc that have capability to form film on the exterior of metals cannot be used.

iii) Passivating (anodic) inhibitors retarders: These type of inhibitors are also known as anodic inhibitors inhibit corrosion by reducing the flow of current in an electrochemical system. This inhibitor shifts the potentiodynamic polarization curve. To achieve this shift passivating inhibitor are usually like a coat, that is anti-corrosion paint used to coat the metal. The coating reduces the freedom of metal ions from the exterior of the metal to the solution. Two type of this inhibitor exist and they are oxidizing anions and the non-oxidizing anions. The oxidizing anions hide the metal in the presence of oxygen. Some examples of this include nitrate, nitrite and bromate. The second group are non-oxidizing inhibitors such as phosphate and molybdates. These require oxygen if they must function as passivating inhibitors. Over all, this type of inhibitors has high inhibition efficiency. One major setback with this inhibitor is the need for high concentration. The concentration should typically be more than the critical concentration. If the concentration is lesser it will result into corrosion that is localized, for instance pitting (Lecante et al., 2010).

iv) Film inhibitors: Film forming inhibitors come across as either cathodic or anodic depending on which part of these has more of the film coating. If the film covers cathodic active sites, then it is an anodic inhibitor type of film because the corrosion potential will shift to the anodic direction, making it more negative. While a more film coverage of the anodic sites of reaction is a cathodic film inhibitor because the corrosion potential will shift to the cathodic, that is it becomes more positive. An equal settling of the film on the metal exterior mean that there is an equal coverage of both the anodic and cathodic sites of corrosion reaction on the exterior of the metal such that the shift will be small in both directions (Rocha et al., 2010).

v) Organic inhibitors: All organic compounds used for corrosion inhibition have been found to be composed of polar functions that have heteroatoms (such as oxygen, sulphur and or nitrogen), π electrons and heterocyclic compounds. Researchers have revealed that organic compounds are able to inhibit corrosion because they possess O, S and N heteroatoms (Bentiss et al., 2002). It is the presence of free electron pairs of these heteroatoms, multiple bonds or delocalized pie electrons of aromatic rings with and high molecular weight alkyl sustituent groups that confers the inhibition ability in most plants (Karthikaiselvi and subhashini, 2014; Manimegalai and Manjula, 2015). Most of these inhibitors as synthetic chemicals require rigorous process to synthesize, and hence they are expensive as well. A number of these inhibitors are toxic and hazardous in nature and pose serious threat to humans and the environment at large. Faced with challenges many researchers engage in the search for alternative inhibitors that are not only safe and environmentally friendly but cheap and abundant with renewable resources. This search is of utmost importance for safe and efficient corrosion control in practically all industries (Okafor and Yugui, 2008; Oguzie, 2008a and 2008b). Recent studies by various researchers have proved that extracts from plants can be used as corrosion inhibitors. This type of inhibitors can be efficient replacements for inhibitors that are derived from chromium – such as chrome phosphate, strontium chromate and zinc chromate. These inhibitors back bone are heavy metal and cause cancer in humans. Also, inhibitors in the form of coates that have Lead as the backbone have been found to affect children with several complications hence the need to replace them. Part of the health dangers humans are exposed to include Liver damage, disorders in blood and Kidney failure. These health challenges are common with the use of potassium dichromate or chromic acids in very little quantity. Human lungs are also affected as they are prone to cancer when exposed to Chromate mists from chromium base inhibitors (Umoren et al., 2013).

Corrosion inhibitors from plant extracts

Faced with the dangers of many organic inhibitors to human health researchers delved into alternative source of organic inhibitors that will not affect human health negatively. This search has explored the use of various parts of plants and they have been reported with positive results (Abiola et al., 2009; Abiola and James, 2010; Loto et al., 2013; Oguzie, 2008b; Quraishi, 1999). Over the years, researchers such as Abd-El-Nabey et al. (2006) have reported that components of plants are rich in natural biochemical compounds successfully extracted via very simple processes with minimal cost. They are environmentally acceptable, biodegradable, freely accessible and renewable. Alkaloids, organic nitrogen bases and carbohydrates have been identified as the major inhibiting compounds coupled with proteins and products of their acid hydrolysis. Investigations as the search for natural extracts with the ability to with stand high temperature without degrading are still on. The economic benefit of natural extracts as inhibitors has been well established.

Extent of past work

As seen above, there are various means of corrosion inhibition and these include corrosion retarders not expensive but very effective corrosion control measure for metals exposed to corrosive environments that are aqueous in nature. Again, as stated above, organic inhibitors function by having their molecules stick to the exterior of the metal thereby creating a barricade against the corrosive agents. The inhibition efficiency of these retarders depends chiefly on the chemical/physical configurations and electrical properties that characterize the resulting inhibitor–metal complex. These inhibitor metal complexes will in turn depend on:

i) Original configuration of the inhibitor,
ii) Level of retarder concentration,
iii) Condition of the exterior of metal and number of possible adsorption sites,
iv) The temperature of the metal, corrosive system and
v) The makeup of the corrosive environment.

Use of organic compounds

N-1-naphthylethylenediamine dihydrochloride monomethanolate (N-NEDHME) has been reported as a retarder of of carbon steel in 2 M H_3PO_4 corrosion. The technique used and test temperature was loss of weight and electrochemical potentiodynamic polarization (potentiodynamic polarization or Potentiodynamic polarization) and electrochemical impedance (EI) from 303-328K. Zarrouk et al., (2013) who carried out this study reported that inhibition efficiency (IE%) got better as the retarder concentration enlarged, while a reduction in the IE% was reported with rise in the temperature. The correlation coefficient (R^2) for the Langmuir isotherm model was reported to have provided a better explanation of the adsorption performance of the compound investigated as a retarder of tested coupon corrosion. The Potentiodynamic polarization results show that the investigated compound behaves as a both a cathodic and anodic inhibitor.

Weight loss and EIS were used to investigate the effectiveness of derivative of triazole (PAMT) as a corrosion retarder of mild steel in phosphoric (H_3PO4) acid environment. Li et al. (2012) who carried out this study reported that from the experimental results it can be said that PAMT has a noteworthy influence on the corrosion retardant of the tested coupons in H_3PO_4 solution. They also reported that at higher concentration, PAMT was effective as an inhibitor. The data generated from their experiment shows that PMAT fits Langmuir isotherm model indicating that single molecules of the inhibitor got adsorbed on one active corrosion site at a time. The potentiodynamic polarization results reveals that the triazole derivatives acts as dual retarders in both anodic and cathodic direction and acting predominantly in the cathodic direction. They also reported that both the gravimetric and the potentiodynamic polarization results are in good agreement as to the effectiveness of the PMAT triazole derivative.

Yadav et al. (2012) tested capability of four different benzylidine malononitriles (BMNs) compounds on mild steel corrosion in a 1 M HCl with like Energy Dispersive X-ray (EDX), gravimetric, EIS, scanning electron microscopy (SEM) and Potentiodynamic polarization techniques to investigate the corrosion inhibition. The resulting data from the experiment were fitted into different isotherm adsorption models with a correlation coefficient that favoured the model of Langmuir as the best fit that describes the adsorption process of the four compounds under review. The surface of the tested coupons was analyzed with SEM and EDX, and the result reveals a protective film of the retarder on the exterior of the metal. Also they reported that their experimental results when compared with the quantum chemical calculations correlated very well.

Gopiraman et al. (2012a) explored the corrosion inhibition proficiency of six different synthesized Benzoyl compounds namely (1) 1-Benzoyl-3,3-diphenylthiourea, (2) 1-benzoyl-3,3-dibenzylthiourea, (3) 1-benzoyl-3,3-diethylthiourea, (4) 1-benzoyl-3,3-dibutylthiourea, (5) 1-benzoyl-3,3-bis(2-methylpropyl) thiourea, and (6) 1-benzoyl-3,3-bis(propan-2-yl) thiourea on mild corrosion in 1 M concentration of HCl using chemical and electrochemical measurements. Gopiraman et al. (2012a), reported that all methods used for the test indicate successful inhibition using the compounds as their inhibition efficiencies were measurably good and in agreement although the second inhibitor had a better inhibition percentage performance efficiency. Tafel polarization results for all the tested inhibitors was reported as indicating that the inhibitors are all good. Gopiraman et al. (2012b) also investigated inhibition property of N-(phenylcarbamothioyl) benzamide (PCB) a thiourea derivative in 1 M HCL using gravimetric measurement and electrochemical techniques (Potentiodynamic polarization and AC impedance spectroscopy). The derivative of thiourea was reported to be mixed type inhibitor. The temperature data revealed that the adsorption obeyed Langmuir isotherm of adsorption with a Gibbs free energy of adsorption that indicate both physical and chemical attachment of retarder molecules on the mild steel surface. Gopiraman et al. (2012b) confirmed the adsorption mechanism for all inhibitions using ultraviolet–visible Fourier transform infrared (FTIR), SEM–energy-dispersive X-ray (SEM–EDX) and Raman, and spectroscopic methods.

Studies on the inhibition performance efficiency of the following pyrazine derivatives (1) 2-methylpyrazine (MP), (2) 2-aminopyrazine (AP) and (3) 2-amino-5-bromopyrazine (ABP) on the corrosion of cold rolled steel (CRS) immersed into a corrodent solution of 1.0 M H_2SO_4 by gravimetric measurement, electrochemical techniques namely Potentiodynamic polarization curves and EIS methods. The results as reported by Xianghong, Shuduan and Hui (2011), shows that pyrazine compounds are good inhibitors, with the best of the three in terms of inhibition efficiency being ABP, then AP and MP. The adsorption of ABP, AP and MP inhibitors on the exterior part of CRS was reported to have agreed with adsorption isotherm according to Langmuir, the Potentiodynamic polarization studies proves that they are all mixed-type inhibitors.

Shylesha et al. (2011) scrutinized the inhibiting strength of 2 – methyl -3- (trifluromethyl) aniline on the corrosion of mild steel immersed in 1 M HCl and 0.5 M H_2SO_4 solutions using weight loss and electrochemical technique of investigation. The performance of the inhibitor is said to be concentration dependent in the aggressive solution while the use of Electrochemical technique in the studies showed that the inhibitor is a dual or mixed type with a slight affinity towards anodic reaction. The inhibitive performance of the inhibitor in HCl were better than the result in H_2SO_4.

The inhibitive capability of thiourea to retard corrosion of Armco iron immersed in 0.5 M Hydrochloric acid corrodent as examined using Potentiodynamic polarization and EIS procedures. Awad (2004) who carried out this investigation reported that the effectiveness of the thiourea improved with increase in concentration, which decreased after it reached a maximum [around 1 mM]. The temperature data were reported to have obeyed Frumkin isotherm model with lateral or sideways repulsion, such that the molecules are vertically adsorbed on the iron exterior using S atom as the link with the empty d-orbital. Also, Awad (2004) reported that Thiourea under critical concentration behaves as cathodic and also anodic inhibitor.

Research studies has been done to see the inhibiting of mild steel corrosion where there is N-[morpholin-4-yl(phenyl)methyl] benzamide (MPB). The concentration of the aggressive environment tested and reported was 1M Hydrochloric acid using mass depreciation, Potentiodynamic polarization measurement and EIS analytical technique. Jamal and Sathiq (2010) presented experimental results that revealed that the inhibition percentage performance improved with every rise in concentration of MPB. They reported that increase in temperature negatively affected the inhibitor percentage performance. The temperature data for the different concentrations of MPB when fitted to isotherm models obeyed the Temkin isotherm adsorption model while the report shows that the Potentiodynamic polarization curve analysis reveals a dual type inhibitor for the retardant actions of MPB in HCl environment.

There have also been studies on antipyrinyl derivatives 4 and 5 as retarders of mild steel corrosion. As reported by Mahmound and Khaled (2015), these retarders of corrosion were synthesized from enaminonitrole 3 with 1-nitroso-2-naphthol and salicyaldehyde reaction. The efficacy of the compounds were examined with gravimetric analysis, Potentiodynamic polarization and EIS measurements. Their published data reveals that the inhibitors are effective mild steel corrosion retarders. The effectiveness of the retarders are related to the retarder molecules ability to block sites of corrosion reaction on the tested coupons surfaces. The results affirmed that the inhibitors action is dual i.e. cathodic and anodic retarders.

The capability of 4-amino-5-phenyl-4H-1, 2, 4-trizole-3-thiol (APTT), ethylenediamine tetra-acetic acid (EDTA) and thiourea (TU) to inhibit mild steel corrosion in 1 M HCl corrodent at ambient temperature was explored by Musa et al. (2010) who undertook this study used Tafel polarization and EIS. They reported that the various inhibitors performance are concentration dependent as the IE% enlarged with rise in APTT, EDTA, and TU concentration. Also, Musa et al. (2010) and his co-researchers reported that the free energy of adsorption (ΔG_{ads}) suggests an impulsive reaction procedure that is likely chemisorption in nature for the molecules of the inhibitors while the molecules of APTT, EDTA, and TU adsorption on the tested coupon surface fits adsorption isotherm model according to Langmuir.

The capability of 3-pyridinecarboxaldehyde thiosemicarbazone (META) as a mild steel corrosion inhibitor in 1 M HCl was examined by Khaled et al. (2010). They used mass depreciation, Potentiodynamic polarization and EIS to monitor the performance of META as an effective retarder of corrosion of the tested coupons in 1 M corrodent solution of hydrochloric acid and recorded an inhibition efficacy above 94% at 0.01 M concentration of the inhibitor considered as the highest. They reported that the reaction between the extract and the tested coupon surface was feasible themodybanically speaking and that the molecules of 3-pyridinecarboxaldehyde ot adsorbed either chemically or physically while the correlation of the plots of concentration against temperature gives data that fits Langmuir adsorption isotherm. Potentiodynamic polarization results as reported shows that the molcules favored both anodic and cathodiic direction. Also, the SEM analysis is reported to indicate the adsorption of 3-pyridinecarboxaldehyde molecules at the tested coupon and solution interface.

A thorough investigation of the effectiveness of Torsemide and Furosemide drugs as corrosion retarders of mild steel in 1 N HCl was carried out by Sappani and Sambantham (2013) using gravimetric and electrochemical methods. The inhibition efficiencies result of Torsemide and Furosemide drugs obtained using weight loss agree with the result from polarization studies. While it was reported that Torsemide exhibited higher inhibition efficiencies than Furosemide, the Potentiodynamic polarization results showed that the compounds retardered corrosion at anodic and cathodic regions and corrosion activities in both anodic and cathodic sites reduced substantially. They reported compliance with Langmuir adsorption isotherm while their FTIR and UV reports confirmed development of Fe–inhibitor which agree with FT-IR result. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) results proved that a defensive layer was made on the exterior of the mild steel.

Another drug that has been investigated as inhibitor is Cefuzonam (CZM). Singh, Ebenso and Quraishi published a report on the use of the drug CZM as corrosion inhibitor in 2013. Their investigation focused on the adsorption behavior of CZM on the exterior of tested mild steel using measurement of the contact angle of the acid solution on the tested steel, mild steel. They reported that the contact angle of increased as concentration of CZM was increased. This report confirmed the theory that with CZM as inhibitor the tested coupon surface became more hydrophobic. The gravimetric and electrochemically studies – which were basically EIS and Tafel polarization (TP), results agree that inhibitor molecules adsorbed on the tested coupon surface by electron giver and acceptor collaborations that occurred amongst pie - electrons in the double bonds of benzene as a pendant group and the heteroatoms S and N and the iron atoms unoccupied d-orbital. The data fitting of the experimental result into the various isotherm models to identify the isotherm model that gives the best description of the adsorption of the CZM was found to align with adsorption isotherm of Langmuir which means that every active site was covered by a molecule of CZM. Singh et al. (2013) reported that CZM is a dual type inhibitor going by the Potentiodynamic polarization data.

Obot et al. (2013) studied the possibility of using Xanthione abbreviated as XION in the retarding of the tested coupon disintegration in sulphuric acid environment. They reported that their interest in use of XION as corrosion inhibitor was due to the compounds possession of multiple pi electrons on its structure. Using 0.5 M sulphuric acid at kelvin temperature range of 303–333 K as the corrodent solution and temperature respectively they examined the possibility of XION getting adsorbed and retarding corrosion of the tested coupons by weight loss and visible spectrophotometric (UV) tests. From collated data they reported that XION is a very good inhibitor of tested coupons corrosion in H_2SO_4 and they recorded and reported a 98.0% notable low XION concentration of 10 micro M. While Obi and Obot reported that IE% was increased with increase in concentration of XION and decreased as the temperature increased up to 333 K indicating a likelihood of physisorption, they also suggested the adsorbsion was according to Langmuir isotherm. Formation of a complex of XEN–Fe was confirmed using UV–visible absorption spectra, meaning that for a corrodent with XION a complex that retards corrosion is formed with the tested coupon.

Jafari et al. (2014) examined the possible use of 2-Mercaptobenzothiazole (MBT) and 2-aminobenzothiazole (ABT) compounds as corrosion retarders for ST-37 carbon steel in 1M HCl solutions. They conducted the study using EIS and confirmed that the two compounds served the purpose of corrosion inhibition in the system. Atomic Force Microscopy (AFM) examination was reported to have shown that MBT was a better inhibitor of carbon steel dissolution in 1 M HCl when compared to ABT.

Ayssar et al. (2012) synthesized 3-benzoylmethyl benzimidazolium hexafluoroantimonate compound and tested same in aggressive solution to see their efficacy. They conducted the study using EIS and depreciation of methods. The tested inhibitor concentration ranged from 5×10^{-7} M to 5×10^{-4} M. The temperature effect for an increase in temperature from a kelvin temperature of 303 to 343 K was examined also. The resulting data revealed that, inhibition effectiveness improved as inhibitor concentration was increased. They reported the obvious situation that inhibition performance decreased as temperature increased and the presence of the heteroatom N in the benzimidazole explains the reason for observed effectiveness of the inhibitor. This also applies to phenyl ring.

Gao et al. (2010) conducted a study on 8-hydroxyquinoline (8HQ) and sodium dodecylbenzenesulphonate (SDBS) effects as inhibitions of the corrosion of AZ91D magnesium alloy in severe corrodent solution using EIS and Potentiodynamic polarization tests. The results show that for SDBS, the significance of the retarders effect was not pronounced. For 8HQ, a rise in inhibitor efficacy was reported as dependent on the time the tested coupons stayed in the corrodent solution, and the constituent of the film was $Mg(8HQ)_2$. Upon mixing 8HQ and SDBS inhibitors, a synergistic inhibition behavior was observed, and the mechanism for a proper cooperative action between the retarders was proposed.

Parameswari et al. (2010) studied the effect of benzoisoxazole and benzopyrazole derivatives as inhibitors in retarding mild steel corrosion in H_2SO_4 environment. They used weightloss, Potentiodynamic polarization, EIS and SEM analysis. All the four compounds did very well as retarders corrosion of the tested coupons in H_2S0_4 anda a more than 90% EI% at 0.6 mM at 298 K was attained. Adsorption obeys Langmuir adsorption isotherm and are dual type of inhibitors as seen in Polarisation investigations.

Okafor et al. (2009) studied the inhibition of N80 mild steel disintegration in CO_2 - saturated 3% NaCl solutions with or without 2-undecyl-1-ethylamino imidazoline (2UEI) using Potentiodynamic polarization and EIS techniques. The structure of the N80 mild steel studied was characterized with SEM. For this investigation they reported that the increase in concentration of 2UEI lead to rise in EI%. Also the results of temperature test carried indicate that there was rise in EI% when temperature was increased against drop in the activation energy (E_a) of the corrosion process with 2UEI present. They also explored adsorption characteristics of 2UEI as a metal dissolution retarder and the results as published proposed that 2UEI got adsorbed on the tested coupon via chemisorption process, while adsorption isotherm that best describes the process is the Temkin isotherm. The result of the presence of iodide ions shows that iodide ions improved the performance of 2UEI meaning that the synergism was effective.

Mild steel dissolution control in 1 M HCl with two different alkylimidazolium based inhibitors namely 1-butyl-3-methylimidazolium chlorides (BMIC) and 1-butyl-3-methylimidazolium hydrogen sulfate ([BMIM]HSO_4) was investigated by Zhang and Hua (2009). Zhang and Hua used EIS, Potentiodynamic polarization and weight depreciation measurements in their study and found that [BMIM]HSO_4 is better compared to BMIC. They reported from the result of Potentiodynamic polarization that the inhibitors are mixed type inhibitors that retard dissolution of metal at the anode and retard the evolution of hydrogen from cathodic reaction. The inhibitors were also found to have an improved performance as their concentrations were increased indicating that they are concentration dependent. The correlation coefficient results affirm that the adsorption of the corrosion retarder on the tested coupons surfaces are best described by Langmuir's adsorption isotherm.

The inhibitory capability of N,N′-Methylenediacrylamide (NNMA) was investigated by Avci (2008) using Potentiodynamic polarization, EIS and polarization resistance measurements. This capability check was conducted on mild steel corrosion in 0.5 M Hydrochloric acid environment Avci (2008) reported that a rise in the concentration of NNMA gave rise to increase in IE% while the Potentiodynamic polarization result that NNMA reduced corrosion in anode and cathode active sites with more leaning toward the cathodic direction. He also reported that the inhibitor molecules got attached on the tested coupons in obedience to Langmuir isotherm of adsorption. The E_a results showed that the adsorbed molecules of the inhibitor NNMA form a film that block charge and mass transfer that result in dissolution of the mild steel metal and hydrogen evolution, a reduction reaction.

Dubey and Singh (2007) studied the capability of Polyethylene Glycol Methyl Ether (PEGME) preventing dissolution of mild steel in a corrodent of one normal sulphric acid. They directed their research on the relationship between inhibitor concentration and the temperature. Galvanostatic and potentiostatic polarization techniques were employed. Results show that PEGME successfully inhibited mild steel corrosion in acidic environment. Dubey and Singh revealed that every increase in inhibitor concentration gave rise to increase in the IE% which did not change as temperature increased.

James et al. (2007) extended the search for corrosion inhibitor to the use of Pyridoxol hydrochloride (PXO). PXO was used as a retarder of mild steel corrosion in a corrodent of 2 M hydrochloric acid. PXO exhibited a considerable inhibition efficiency as its concentration increased at ambient temperature (303 K) as seen in the weight loss analysis result reported. They reported a first order reaction and a leaning towards physiosorption process. Again they reported that the results obtained from weight depreciation analysis and hydrogen evolution reveal that PXO is effective hydrochloric acid. Also the results of the data fitting show that PXO obeys Langmuir adsorption isotherm hence it is the adopted isotherm model for PXO.

Use of polymer as inhibitors

Bouklah et al. (2006) ventured into the synthesis of new corrosion retarders called 1-{2-[(2 hydroxyethyl)thio]ethyl}pyrrolidin-2-one (P5) and {[2-(2-oxopyrrolidin-1-yl)ethyl]thio}acetic acid (P4),. P4 and P5 were verified using steel immersed in strong acid. Authors compared the functionality of P4 and P5 to their initial compounds 1-vinylpyrrolidin-2-one (P1), 2-mercaptoethanol (P2) and mercaptoacetic acid (P3) using linear polarisation resistance (Rp), loss in weight calculations, Potentiodynamic polarization and EIS. The findings as reported reveal that P5 achieved high inhibition percentage performance at a 5 x 10^{-3} M inhibitor concentration of. the results of all the methods employed were in unison, while the Potentiodynamic polarization showed that pyrrolidones acted as cathodic inhibitors with an activating mechanism reduction of proton at the steel exterior. The fitted data showed that P4 and P5 followed Langmuir adsorption isotherm model. The acid used was 0.5 M H_2SO_4.

Another compound of interest that has been researched on is 2-mercaptobenzothiazole (MBT). The effect of this compound on steel type - API 5L X52, corrosion in 1 M sulphuric acid corrodent was investigated by Majid et al. (2013) using electrochemical and theoretical methods. MBT was reported by Majid et al. (2013) as a very good retarder of steel corrosion in especially H_2SO_4 environment. While the IE% was reported to have increased with the rise in MBT concentration, the thermodynamic adsorption parameter reveal that MBT got adsorbed via both physical and chemical adsorption processes and the data fitted and obeyed Langmuir adsorption isotherm.

Mohammed et al. (2010) studied the effectiveness of three amino acids as inhibitors of iron corrosion in 1 M HCl corrodent environment using Tafel polarization, impedance measurements, Molecular dynamics (MD) and some other theoretical studies like Density Functional Theory (DFT). The result as published shows that the amino acids - alanine (Ala), cysteine (Cys) and S-methyl cysteine (S-MCys) were sufficiently effective. While Cys and S-MCys retarded corrosion in both cathodic and anodic directions, Ala reduced corrosion in the cathodic direction alone. By inference they observed that Cys, was more effective in retarding the iron corrosion than both Ala and S-MCys essentially because its molecular structure has a mercapto group and that S-MCys ranked next in the other of effectiveness with Ala being the least of all. The lag in the effectiveness of inhibition reported for S-MCys when compared against Cys and effect is credited to steric effects associated with methyl substituent on the mercapto group attached to S-MCys. Again they compared the Tafel extrapolation method results with inductively coupled plasma atomic emission spectrometry (ICP-AES) and Electrochemical frequency modulation (EFM) technique results, and the comparison showed that the Tafel extrapolation were correct hence the corrosion rate recorded in the presence of Cys, S-MCys and Ala in the corrosive environment was validated as they very well agreed with measurement done using EFM and ICP methods. Mohammed et al. (2010) reported establishing a correlation between both electronic and molecular structures of Cys, MCys and Ala and their various inhibition efficiencies through theoretical studies such as MD and DFT. Overall they reported that the amino acids experimental and theoretical studies all agree that they were useful inhibitors and hence effective.

Inhibitors from water soluble polymers

Karthikaiselvi and Subhashinis (2014) investigated the inhibition efficacy of (Vinyl alcohol-o-methoxyl aniline) PVAMOA as corrosion inhibitor for mild steel corrosion in 1M Hydrochloric acid solution using gravimetric, Potentiodynamic polarization and EIS methods. This polymer is novel and water soluble. The IE% results determined by weight loss agree with the results of electrochemical measurement indicating that PVAMOA is a good corrosion retarder. The IE% was observed to decline with rise in temperature.

Xiumei et al. (2013) explored the inhibitive properties of 1, 4-bis (benzimidazolyl) benzene (BBMB) a compound of bisbenzimidazole on the corrosion of mild steel in 0.25 M sulphuric acid solutions and 0.5 M Hydrochloric acid solution also. Potentiodynamic polarization and EIS methods were used in the investigation. Also, the weight loss of the metal coupon was monitored for variation. The methods of test employed in this case showed that BBMB is a good corrosion retarder in H_2SO_4 and HCl.. It was observed from the results that BBMB was better in 0.5 M HCl solution than in 0.25 M H_2SO_4 solution. Xiumei et al. (2013) fitted the values of the adsorption of BBMB on the tested coupons surface using the tested acid concentration and they aligned with Langmuir adsorption isotherm in the different tests. Potentiodynamic polarization curves identified BBMB acting as both cathodic and anodic retarders of corrosion through both reduction of the anodic tested coupons dissolution reaction and inhibiting the hydrogen evolution reaction.

Cationic surfactants derived from olyel-amido were investigated as carbon steel corrosion retarders in Hydrochloric acid environment. Zaafarany (2013) used gravimetric and electrochemical polarization tests to determine the efficiency of the cationic surfactants, the reported result shows that the level of inhibition in percentage increased with rise in the concentration of the tested corrosion retarders and decreased as the temperature of the corrodent solution (that is the test medium) increased. It is also reported that when the polyethylene diamine unit increased the inhibitor performance also increased. The best fit isotherm model is the Freundlich model of adsorption isotherm. The Potentiodynamic polarization curve shows that the corrosion potential was in the anodic direction. The report identified the type of corrosion involved as a pitting corrosion.

Prathibha et al. (2013) using gravimetric and electrochemical experiments coupled with scanning electron microscopy characterization investigated the inhibition strength in percentage of Tetra-n-butylammonium bromide (TBAB) on mild steel corrosion in H_2SO_4 environment. The weight loss, Potentiodynamic polarization and EIS results all indicate that TBAB was effective in controlling the mild steel corrosion. In addition to the above Prathibha et al. (2013) reported that the Potentiodynamic polarization reveals TBAB is a dual function inhibitor with an IE% that increased when the TBAB concentration increased and declined when the temperature of the electrolyte increased also. They capped their findings with the report that TBAB obeys Langmuir adsorption isotherm as all experimental data fitted well giving a correlation coefficient that approximates unity.

Use of organic dyes as inhibitors

Ebenso and Oguzie (2005) and Oguzie (2005) examined the possibility of using some organic dyes namely; safranine –o (SO), thymol blue (TB) and Fluorescein –Na (F-Na) as corrosion inhibitors of mild steel corrosion in sulphuric acid. In each of the studies they used gasometric technique which revealed that the compounds act as corrosion retarders in acidic environment. Their report shows that upward increase in concentration of SO and TB resulted in IE% increase.

The ability of another dye, Methylene blue (MB) dye to inhibit corrosion of aluminium in HCl electrolytic solution was studied using gravimetric techniques at 303 and 333 K. Oguzie et al. (2005) who engaged in this research revealed that MB acts as an inhibitor in the acidic corrodent. They reported that the inhibition efficiency is dependent on concrentration of the acid and that of MB. As with many other inhibitors the inhibitor performance increased as the concentration of MBT increased, and MBT was reported to follow physiosorption mechanism. It is also reported that when KCL and KBr halides were added the IE% increased. The activation energy values support a physical absorption process for MBT on the Aluminum surface.

Mirghasem et al. (2003) investigated the corroding retarder effects of sodium dodecylbenzenesulphonate (SDBS) and hexamethylenetetramine (HA) on the corrosion of mild steel immersed in sulphuric acid solution. The study was conducted using Tafel polarization, weight loss, and EIS. Their findings show that HA's performance as an inhibitor depended on its concentration. SDBS on the other hand was reported to show optimum percentage inhibition performance when the concentration was about 250 ppm, and this related to the formation of hemi-micellar aggregates that increased the corrosion retarder desorption from the metal/solution interface at higher concentrations. A synergistic effect is observed when HA and SDBS are mixed with clear regions of synergistic and antagonistic behaviors were observed and this is suggested to be due to electrostatic relations amongst them. Both inhibitors are reported to follow Langmuir and Frumkin isotherms.

Bentiss et al. (2002) studied the corrosion retarding capability of 2,5-bis(n-methoxyphenyl)-1,3,4-oxadiazoles (n-MOX), for mild steel in 1 M Hydrochloric acid and 0.5 M sulphuric acid by measurement of weight loss and electrochemical methods. Bentiss et al. (2002) posited that at low concentration of n-MOX a favourable corrosion inhibition was observed. They also reported that among the oxadiazoles studied, the best performing corrosion retarder was 2-MOX with its best performance reported in 1 M HCl compared to its performance in 0.5 M sulphuric acid. Again 2-MOX in 1 M HCl behaved like a cathodic and anodic corrosion retarder as seen in the Potentiodynamic polarization curves, while in 0.5 M H_2SO_4, the inhibition mode of 2-MOX is said to be dependent on the electrode potential and acts essentially as a cathodic inhibitor. They also opined that inhibition efficiency increased slightly as the temperature increased from 25 to 60 ^oC. The temperature data upon addition of 2-MOX fitted well into Langmuir isotherm model and decreased the activation energy of the system.

Some past investigations on corrosion inhibition by extracts from plants

The search for natural products of plant origin to be used as corrosion inhibitors because they are inexpensive, eco-friendly and have a wide variety of compounds for corrosion retarders has become an area of study with much interest. The inexpensive and non-toxic extracts from plant leaves, barks, seeds, fruits and roots contain organic constituents with molecular structures containing, P, N and or O atoms. They are richly available and renewable resources of corrosion retarders coupled with their intricate structure of biomass extracts, which have characteristic similar to that of synthesized for corrosion inhibitor.

Sheeja and Subhashini (2014) investigated the possibility of using *Pavetta Indica* (PI) leaf extract as an inhibitor to prevent mild steel corrosion in HCl and H_2SO_4 environment. They worked with weight loss and electrochemical technique in their study and found out that acid extracts of PI leaf actively retard the corrosion of mild steel. They reported that acid extract of PI leaf are concentration dependent as their IE% increased along with an increase in concentration of PI leaf. Again, they classified PI leaf extract as a mixed type inhibitor following Potentiodynamic polarization investigation with no change in the reaction mechanism of hydrogen evolution and using impedance parameters they affirmed that biomaterial got adsorbed on the mild steel surface hence forming a protective film that increased as the immersion time increased.

In another study, Alaneme and Olusegun (2014) synthesized Succinyl amide gemini surfactant herein represented as SAGS from the seed oil of *Adenopus breviflorus.* The process of extraction was authenticated using NMR and FTIR analysis. The synthesized SAGS was used as a mild steel corrosion inhibitor in 0.5 M HCl with weight loss method, SEM analysis, emulsion stability, surface tension and wetting power employed as investigation channels. They reported that there was an exothermic spontaneous adsorption of SAGS and temperature experiment results that fitted well into Langmuir adsorption isotherm and the adsorption process adjudged a physisorption process. They concluded that SAGS extracted from *Adenopus breviflorus* is an efficient inhibitor of the tested coupon corrosion in 0.5 M Hydrochloric acid solution, and compared satisfactorily with other Gemini surfactant systems.

Inhibition effect of Chlorophytum borivilianum root extract (CBRE) on mild steel corrosion in 1 M HCl and 0.5 M H_2SO_4 environment was studied with various techniques such as depreciation of weight, EIS, Tafel polarization, and SEM analysis. It is reported that a rise in inhibitor concentration lead to increase in IE% in all tested acid environment. They also examined the effect of duration of coupon immersion in the corrodent solution, the change in temperature and concentration of the acid solution on the functionality of CBRE. Following temperature test they recommended that the retarder aligned with Langmuir isotherm model as the adsorption isotherm that best describes it. UV–visible study and SEM affirmed the molecular adsorption of the extract on the exterior of the tested coupon. It is obvious that the techniques results are in agreement and affirm that the extract is a suitable corrosion inhibitor of the tested coupon in the acids environments (Gopal et al., 2013).

Sribharathy and Rajendran (2013) studied the inhibitive properties of extracts of Jeera (*Cuminum cyminum*) plant on the corrosion of mild steel in an aqueous solution of seawater using Potentiodynamic polarization and EIS methods. The stability of the IE% of extracts of Jeera was examined by weight loss method. Potentiodynamic polarization curves indicated that the Jeera extract behavior was anodic in nature. EIS measurements showed that the dissolution process occurs under activation control. The corrosion rates of steel and the inhibition efficiencies of the extract obtained from impedance and polarization measurements were in good agreement. Inhibition was found to increase with increase in concentration of the plant extract. The results indicate that Jeera extract are possible corrosion retarders for mild steel exposed to seawater.

Umoren et al. (2013) conducted a study on the possibility of using extracts of *Phoenix dactylifera,* that is Date palm seed as a retarder of mild steel corrosion in 1 M Hydrochloric acid and 0.5 M sulphuric acid solutions by loss of weight and electrochemical methods. Umoren et al. (2013) concluded that IE% of Date palm seed extracts increased or decreased depending on whether the extract concentration increased or decreased as the temperature of the experiment increased. The duration of immersion was also found to influence the corrosion inhibition effect in two different acid media while the polarization curves showed that the Date palm extracts functioned as a dual type inhibitor that controlled both the cathodic and anodic sites where oxidation and reduction corrosion reactions took place. The data fitting returned positive for Langmuir adsorption process for the extracts adsorption onto the mild steel surface used in the investigation. Umoren et al. (2013) concluded that Date palm seed extract is a good corrosion inhibitor for the tested coupon mild steel in 1 M Hydrochloric acid compared to a 0.5 M H_2SO_4 solution.

Pandian et al. (2013) investigated on the possibility of the use of *Neolamarckia cadambacrude* bark and leaves extract and pure alkaloid (3b-isodihydrocadambine) as corrosion retarders for mild steel corrosion in 1 M HCl medium. Potentiodynamic polarization, EIS, SEM, FTIR spectroscopy and molecular modeling were employed in this investigation. Their results showed that the crude extracts and 3b-isodihydrocadambine reduced the corrosion rate significantly at all concentrations. Potentiodynamic polarization measurements indicated that these green inhibitors acted through mixed type inhibition. SEM investigation proved that there was formation of a protective film over the surface of the tested coupon while FTIR, supported by molecular modeling affirmed that this defensive effect was caused by alkaloids, particularly 3b-isodihydrocadambin.

Pradeep and Mohana (2013) chose to examine the possibility of using extracts of Plumeria rubra (PR) as corrosion retarder for mild steel immersed in industrial water. To conduct this research, they used weight loss, potentiodynamic polarization and EIS techniques. Pradeep and Mohana (2013) reported that the IE% increased as the inhibitor concentration changed in the positive numbers and reduced as temperature increased. The system charge transfer resistance measured with EIS was reported to have increased as the retarder concentration became elevated while the adsorption of PR extracts on the tested coupons surface were also reported to fit Langmuir isotherm model of adsorption. Using Potentiodynamic polarization investigation they reported that PR extracts act as a dual type inhibitor namely cathodic and anodic. SEM analysis turned out with impressive surface morphology showing that PR got adsorbed and formed film on the metal surface.

Chen et al. (2013) worked on leave extracts of *Ginkgo biloba* as a substitute for expensive and toxic organic and inorganic inhibitors. They used Q235A steel in their experimental work with analytical tools such as weight loss and Potentiodynamic polarization. They found out that the inhibition efficiency of *Ginkgo biloba* leave extracts are concentration dependent and that the corrosion occurred basically by adsorption with a leaning towards mixed type inhibitor.

Musa acuminata bract were used as retarders of corrosion by Gunavathy and Murugavel (2013) who examined the inhibition efficiency of acid extract of dry *Musa acuminata bract* as a corrosion retarder for mild steel in 1 N hydrochloric acid using experimental methods such as weight loss and Electrochemical methods (Potentiodynamic polarization and EIS). The findings show that IE% increased with rise in inhibitor concentration and decreased with increase in temperature suggesting the occurrence of physical adsorption. The Potentiodynamic polarization curves proved that the inhibitor performed as a both cathodic and anodic type of inhibitor, while the EIS study showed a reduction in dual layer capacitance following the inhibitor adsorption that lead to changes in the structure of the electrode-solution boundary thereby regulating the dissolution of the tested coupons by the mechanism of charge transfer.

Extract of *Osmanthus fragran* leaves (OFLE) as corrosion inhibitor for C-steel corrosion in HCL was studied by Li et al. (2012). In that study they performed experiments using and analysed resulting data using Potentiodynamic polarization, EIS, atomic force microscopy (AFM), FTIR and quantum chemical calculations. The Potentiodynamic polarization result as presented disclosed that OFLE acts as dual type inhibitor while the adsorption type after fitting of temperature data showed it fitted well into Langmuir adsorption isotherm revealing adsorption thermodynamic parameters suitable for a spontaneous exothermic process that is attended by entropy increase. The adsorption behavior was further clarified using calculated Quantum chemical parameters (HOMO, LUMO, Energy gap values and binding energies)

A common green plant-*Vernonia amygdalina* otherwise known as - bitter leaf was put to test by Loto et al. (2013). They used the extracts of *Vernonia amygdalina* (VA) as inhibitor to monitor the corrosion tendencies of mild steel reinforcement bars used in concrete reinforcement. They used Weight loss, pH and electrochemical potential measurement methods in the analysis. Following the standard methods of gravimetric analysis and the resulting corrosion rate calculations they concluded that the green plant *VA* is a good inhibitor of the corrosion of rebar's used in reinforcing concretes. Two-factor ANOVA test was analysed with 95% confidence that revealed that at varying concentration of the tested extract VA and immersion times significantly affected the corrosion potential of embedded steel reinforcement bars in concrete and the pH of the medium (Al Banna et al., 2020; Awwad and Amer, 2020; Awwad et al., 2020a; Awwad et al., 2020b; Igwe and Nwamezie, 2018; Remya et al., 2017).

Earlier Hu and Halil (2006) had shown that extracts of *Schinopsis lorentzii* is a good corrosion retarder for low carbon steel in Hydrochloric acid media. They carried out the study using electrochemical analysis for samples of low carbon steel immersed in 1 M HCl solution in the presence and absence of varying concentrations of *Schinopsis lorentzii* extract as the inhibitor. From their test result they found extracts of *Schinopsis lorentzii* behaved as an inhibitor that depended on its concentration at any point in time during immersion and having a leaning towards cathodic reaction inhibitor and an inhibitor performance efficiency that increased with increase in extract concentration. The adsorption of the molecules of the extract on the low carbon steel surface was in accordance with the Temkin adsorption isotherm.

The use of *Peach juice* as corrosion retarder for mild steel exposed to HCl environment was investigated by Aprael et al. (2011). In their work they subjected samples of mild steel in HCl at different test temperatures up to 50°C using weight depreciation and Potentiodynamic polarization techniques. They reported that inhibition efficiency increased with a rise in test temperature of the corrodent and increase in concentration of *Peach juice* inhibitor concentration. At elevated temperatures above 50°C the inhibitor performance efficiency decreased. Aprael et al. (2011) categorized the inhibitor as one that gets physically adsorbed on the metal substrate following Langmuir adsorption isotherm process since the temperature data indicate a spontaneous formation of a monolayer of inhibitor particles on the metal surface.

The inhibition of low-carbon-steel corrosion in 1 M hydrochloric acid and 0.5 M sulphuric acid by extracts of *Dacryodis edulis* (DE) was examined by Oguzie et al. (2010) using weight-loss measurement and electrochemical techniques. The result demonstrates that the extracts of DE performed as an active retarder of the corrosion of carbon steel in aggressive media. The Polarization studies suggests that the inhibitor is a dual inhibitor while the increase as reported in the impedance spectra confirmed that the organic extract species got attached on the exterior of the carbon steel. The adsorption performance, as approximated by the Langmuir isotherm, shows distinct discrepancies going from low to high DE concentration in 1 M Hydrochloric acid. This situation was correlated with a transition from physisorption at lower concentrations to chemisorption at sufficiently high concentrations. This explanation agrees with the known behavior of inhibition efficiency in relation to temperature and values of activation energy.

Another investigation of interest was that performed by Singh et al. (2010). They investigated the use of seed extracts of *Karanj* (Pongamia pinnata) as a retarder of mild steel corrosion in 1 M HCl environment. They conducted the study using weight loss, EIS, Potentiodynamic polarization, and linear polarization techniques and reported that the seed extracts of *Karanj* (Pongamia pinnata) are useful replacement for inorganic and organic inhibitors that are expensive and toxic. They also reported that when the concentration of the extracts was increased the inhibitor performance also increased and upon further examination the effect of change in temperature, exposure time, and the concentration of the acidic environment on the capability of the extracts as an inhibitor of the tested coupon in 1 M HCl the result was appreciable. Their findings reflect that the extract adsorption process on the tested coupon surface aligned with Langmuir isotherm of adsorption with the particles showing monolayer adsorption process. All the techniques used in the analysis resulted in percentage inhibitor performance that agrees quite well indicating consistency of the extracts as inhibitor.
Also, Singh et al. (2013) categorized the extract of *Karanj* (P. pinnata) seed as a mixed-type inhibitor in HCl environment with an activation energy and other thermodynamic parameters that supported the conclusion. The reported FTIR measurements further reinforced the conclusion that extracts of *Karanj* (P. pinnata) seed formed a monoatomic layer film on the mild steel surface.

The peels of orange and, mango fruits have also been examined to underscore their use as natural sources of inhibitors for corrosion control. Janaina et al. (2014) explored these sources of organic corrosion inhibitors through the study of aqueous extracts of peels of different fruits used as retarders of carbon steel corrosion in 1 M hydrochloric acid solution. Janaina et al. (2014) used EIS, Potentiaodynamic polarization and weight loss methods in their study. They analyzed aqueous extracts of different concentrations of the fruits being studied and reported that the extracts acted as suitable corrosion inhibitors for the tested corrodent solution. As has been reported earlier in several research work on plant extracts as inhibitors of metal corrosion, the IE% increased for every rise in the aqueous extract concentration with a major challenge observed in the decrease of the inhibitor efficiency with increase in the test temperature. However, they reported that Langmuir isotherm model is most suitable model for the aqueous extract adsorption on the metal surface.

Ostovari et al. (2009), carried out investigation on natural products extracted and used as environmentally friendly corrosion inhibitors, e.g. henna extract (*Lawsonia inermis*) and its main constituents (lawsone, gallic acid, -d-Glucose and tannic acid) on corrosion of mild steel in 1 M HCl solution using electrochemical techniques and surface analysis. Polarization measurements indicate that all the examined compounds act as a mixed inhibitor and inhibition efficiency increases with inhibitor concentration.

Lupine (*Lupinous albus L.*) extract is yet another plant extract that has been investigated to determine its efficacy as a corrosion inhibitor of steel corrosion in acidic environment. Abdel-Gaber et al. (2009) investigated the inhibitive effect of aqueous extraction of Lupine in acidic solutions of 1 M H_2SO_4 and 2 M HCl using Potentiodynamic polarization and EIS techniques. Potentiodynamic polarization curves for inhibitive action of Lupine extract indicate it acts as a dual action inhibitor. Again, EIS measurements indicate that the dissolution process is under activation control. The results of the IE% reported from both the Potentiodynamic polarization and EIS analysis agree and suggests that the extract is a suitable inhibitor that is concentration dependent.

In the same year of study conducted by Abdel-Gaber, Eddy (2009) used ethanol extract of Phyllanthus Amarus to develop an inhibitor that served to control mild steel corrosion in sulphuric acid. In his work he measured loss in weight of the metal sample, gas evolution and thermometric methods. As reported in several plant extracts study, the mode of adsorption was physical with the reaction being exothermic and spontaneous in nature for the particles of the extracts got using ethanol.

Okafor et al. (2008) studied the inhibitive action of leaves (LV), seeds (SD) and a combination of leaves and seeds (LVSD) extracts of *Phyllanthus amaruson* mild steel corrosion in HCl and H_2SO_4 solutions using weight loss and gasometric techniques. The results indicate that the extracts functioned as a good inhibitor in both environments and the inhibition efficiency increased with extracts concentration. Elevated temperature investigation indicates an increase in IE% with rise in temperature and there was reduction in activation energies in the presence of the retarder. A chemical adsorption mechanism of the plants components on the exterior of the tested coupon is proposed for the inhibition behavior. The adsorption features were synchronized with Temkin isotherm.

Oguzie et al. (2007c) examined the possibility of the use of extract from Gongronema latifolium as to delay or eliminate corrosion process in aluminum immersed in an acid and an alkaline. To achieve this test, they used 2 M Hydrochloric acid and 2 M potassium hydroxide acid and alkaline respectively. Again they reached the same conclusion that many other researchers have reached which is that every rise in the concentration of the corrosion retarder is accompanied by an increase in the amount of retardation observed. They also classified the inhibitor action on the aluminum surface as being chemical rather than physical adsorption of the organic materials or particles in the acid environment, whereas it is physical in the alkaline environment.

The inhibition effect of *Zenthoxylum alatum* plant extract on the corrosion of mild steel in 5% and 15% aqueous HCl solution was evaluated by weight loss and EIS analysis. It was reported that increase in retarder concentration lead to a commensurate increase in IE%. Also using temperature that varied from 50– 80^{0}C they examined the effect of temperature. SEM, XPS and FT-IR were employed to analyze the surface of the tested coupons. Overall they concluded that retarder reduced the corrosion of steel better in 5% HCl than in 15% HCl, while the inhibitor aligned with Langmuir adsorption isotherm (Chauhan and Gunasekaran, 2007).

Chamomile (*Chamaemelum mixtum* L), Halfabar (*Cymbopogon proximus*), Black cumin (*Nigella sativa* L), and Kidney bean (*Phaseolus vulgaris* L) extracts have also been investigated and reported Abd-El-Nabey et al. (2006). They investigated the capability of these plants extracts to retard corrosion of steel in aqueous 1 M sulfuric acid. In their research work which involved use of EIS and Potentiodynamic polarization techniques. While the EIS measurements revealed that the process of the dissolution of steel happened under activation control the Potentiodynamic Polarization test aligned the behavior of the retarders as dual in nature i.e. cathodic and anodic. Their various IE% revealed them all possible inhibitors for the tested coupons.

Pandian and Mathur's (2008) report on their investigation on the viability of black pepper as a corrosion retarder for mild steel in sulphuric acid was done using weight loss, EIS, Tafel polarization, AC impedance and SEM analysis. They found that the reduction of the corrosion process is primarily due to the presence of alkaloids as essential composites. They stated that an example of this constituents is piperine. The other constituents such as starch, proteins and terpenoids they suggested may work in synergy to increase the strength of the film formed over the metallic surface (Mathur and Pandian, 2008).

Another interesting research on use of plant extracts is the use of *Zenthoxylum alatum* extract as corrosion retarder in different concentrations of orthophosphoric acid. Chauhan and Gunasekaran et al. (2004) who engaged in this research used 20, 50 and 88% aqueous orthophosphoric acid as the corrodent media and exposed mild steel in this media in the presence and absence of *Zenthoxylum alatum* plant extracts. They used loss of weight and EIS in the study and reported that the plant extract functioned better as inhibitor in higher percentage of phosphoric acid concentration. The test units were also exposed to different temperatures ranging from 50–80^{0}C and the best result was reported at 70^{0}C in 88% of the acid environment. Again, using FTIR and XPS, the researchers confirmed adsorption of the extracts on the exterior of the tested coupons.

Al-Otaibi et al. (2014) studied the corrosion inhibitory action of *Lycium shawii, Teucrium Oliverianum, Ochradenus baccatus, Anvillea garcinii, Cassia Italica, Artemisia sieberi, Carthamus tinctorius* and *Tripleurospermum auriculatum* plant extracts on the corrosion of mild steel in 0.5 M HCl using open circuit potential (OCP), Tafel plots and A.C. impedance methods. Al-Otaibi et al. (2014) reported that all the plants extracts demonstrated usefulness as corrosion inhibitors for mild steel in acidic medium and that they are mixed type inhibitors with an open circuit potential lesser than 85 mV required to classify an inhibitor as either cathodic or anodic. Chidiebere et al. (2012) examined corrosion inhibition capacity and adsorption characteristics of Punica granatum extract on mild steel exposed to an aggressive acidic environments using experimental and theoretical studies technique.

Naturally occurring complexes that inhibit corrosion

A number of natural complexes have been identified as responsible for corrosion inhibition capability of plant extracts. These compound include Tannin, Alkaloids, Phenols etc. In separate researches researchers have pinned down on the presence of these compound, for instance Li and Mu (2005), EL-Etre (1998) and EL-Etre et al. (2000) examined the possibility of the use of Beberine, extracts of *coptis chindnsis* and the extracts of *lawsonia* and natural honey as corrosion of mild steel corrosion in 1 M concentration of H_2SO_4 respectively. In these different researches the researchers identified the presence of Tannin, Phenol and Alkaloids containing heteroatoms as basic compounds that provide bonding atoms with the empty d-orbital of the Fe in mild steel.

Pandian et al. (2013) carried out investigation on possibility of controlling corrosion of mild steel in an environment of 1 M HCl using Alkaloid extracted from the leaves (OOL) and bark (OOB) of *Ochrosia oppositifolia*, and *isoreserpiline* (ISR). Electrochemical techniques (Potentiodynamic polarization and EIS) and SEM were employed to analyze the effect of the inhibition properties of the phyto-constituents of the alkaloid extract. Their results indicated that these plant extract inhibitors effectively reduced the rate of corrosion. The Potentiodynamic Polarization and EIS studies revealed that OOL and OOB as inhibitors decreased the corrosion current densities following a mixed-mode mechanism. The SEM observations confirmed the existence of an adsorbed protective film of OOL and OOB extracts with an adsorption process that followed the Langmuir adsorption isotherm. FTIR and molecular modeling employed in the study revealed that the presence of ISR could be responsible for the corrosion inhibition potential of OOL and OOB.

Options for improvement of organic compounds as inhibitors

The researchers have shown that corrosion is a complex process and various plant extracts have proved to be effective inhibitors. However, a combination of inhibitors has also performed very well and in most cases exceeded the performance of single synthesized organic compounds, polymers and plant extracts (Hamilton-Amachree and Iroha, 2020). So, some researchers have combined different organic inhibitors, water soluble polymers and plant extracts and additives to form complex inhibitors (Furman et al., 2020; Harhaun et al., 2020; Manilal et al., 2020; Renu et al., 2020; Sakarikou et al., 2020). As will be seen such blending considers the specific action of the blended inhibitors to achieve a desired complex or compound inhibitor with improved performance, (Oguzie et al., 2007a). One blending that has been quite effective is blending of some organic inhibitors whether synthesized or of natural origin with halide ions. Such blends have produced a blend of inhibitors that effectively control the corrosion process, (Bouklah et al., 2006; Mu et al., 2005; Oguzie, 2004; Oguzie et al., 2007a). A major factor in the effectiveness of this blend of inhibitors is the ability of halide ions to adsorb on metal surfaces undergoing corrosion and creating electrostatic bonding sites that attract the organic inhibitor via Helmholtz electrical double layer, resulting to a supportive adsorption that covers more metal surface in a corrodent solution. This synergy is commonly assumed by researchers as not affecting the chemical structure of the blended inhibitors hence they are simply physical combination. It is therefore basically electrostatic adsorption on the corroding metal surface. This conclusion can be questioned even though no research has. The following are a few such combination of inhibitors and inhibitors with halide ions.

Blend of compounds

Jabeera et al. (2006) carried out research work on the synergism between Tartarate and Tungstate as co-inhibitors in the control of the corrosion of carbon steel in aqueous solutions. Jabeera et al. (2006) used Open circuit potential (OCP), weight-loss and polarization studies in the investigation to understand the corrosion and control activities. They reported that at low concentration of Tartarate ions the synergism was excellent as they recorded high corrosion inhibition performance efficiency which got up to an optimum value of 98% at a mix ration of 500 ppm of Tartarate and Tungstate. This research also revealed that Tartarate has a good passivation effect but did not influence a shift in the surface potential of the metal.

Effect of synergy between organic compounds and iodide

Pavithra et al. (2010) studied the synergism between benzisothiozole-3-piperizine hydrochloride (BITP) and iodide ions on retarding corrosion of mild steel in an environment of 0.5 M sulphuric acid corrodent solution by both chemical and electrochemical methods. The corrosion capability of BITP in 1.0 M Hydrocholric acid and 0.5 M sulphuric acid media was examined and compared. The influence of blending BITP with the iodide ions shows that that there was true synergism. The values of synergism parameter (S) as calculated was greater than unity implying synergism.

Dyes and halides

Some researchers have also investigated the combination of dyes and halides. Oguzie (2004) examined the corrosion inhibition capability of Congo red dye (CR) the dissolution of mild steel H_2SO_4. He reported that CR alone got adsorbed on the metal surface via physical adsorption which change to chemical adsorption when CR acted in synergy with the halides namely KCl, KBr and KI. The heat of adsorption confirmed the chemisorption property of the dye in the presence of the halides.

In another report, Oguzie et al. (2004) evaluated the inhibition capability of methylene blue on Aluminum dissolution in HCl environment. He, (Oguzie, 2005) examined the use of Pigments and resins. Thabo et al. (2015) delved into the use of Sunset Yellow (SS), Amaranth (AM), Allura Red (AR), Tartrazine (TZ) and Fast Green (FG) dyes as corrosion inhibitors for mild steel metal in 0.5 M Hydrochloric acid environment and observed that in the presence of KI the inhibition efficiency of each of the dyes increased. Thabo and coauthors described the success as resulting from the synergy between the dyes molecules and those of the Iodide ions. They also reported that the form pf adsorption in all cases were physisorption with preference for Langmuir adsorption isotherm and then confirmed that the bonding sites were the available heteroatoms (O, N, S) in the inhibitor, that is dye and halide synergy.

Mahmoud and Fouda (2013) conducted a research investigating the use of azo dye derivative (ADD) as a corrosion inhibitor of carbon steel in acidic media - HCl. The IE% was observed and reported to have appreciated with increase in the concentration of the azo dye and all the more so when it was synergized with iodide and bromide ions. The thermodynamic and kinetic parameters data reported after fitting experimental data to Langmuir adsorption isotherm and Arrhenius equation are in agreement with the conclusion reached.

Plant extracts and halides in synergism

Some natural exudate gum has been examined as a likely retarder of mild steel corrosion in sulphuric acid. Umoren et al. (2008) conducted a research in this area of interest using weight loss measurement and hydrogen evolution in a temperature condition that varied from ambient temperature of 30 ^{0}C to 60 ^{0}C. They observed that exudate gum sourced from Raphia hookeri (RH) reduced the rate of corrosion of mild steel exposed to the specific acid corrodent solution and also influenced the inhibition efficiency which increased as the exudate gum content increased close to 5g/l under ambient condition. This gain in inhibition efficiency was lost as the temperature increased. Umoren et al. (2008) revealed that the gum got adsorbed on the tested metal in line with Langmuir isotherm model. They also examined the effluence of halide ions and observed that there was synergy between the exudate gum and the halide ions as the combination of both increased the inhibition efficiency of the resulting inhibitor. In all they suggested physical absorption for the new inhibitor based on the results from temperature test with which the thermodynamic properties and the activation energy was calculated.

Work has been done on the corrosion inhibition of mild steel using seed extracts of *Garcinia kola* (GK), extracts of *Hibiscus sabdariffa* (HS) leafs, *Telferia occidentalis* (TO) leafs, *Occimum viridis* (OV) leafs , and as well as extracts from *Azadirachta indica* (AI) as corrosion retarders in acids commonly used for corrosion tests. 2 M HCl and 1 M H_2SO_4 were employed in this work and the selected method of analysis were gas evolution technique at temperatures that span from ambient temperature of 30 to 60 ^{0}C. Oguzie (2008a) who undertook this study revealed that all the plant extracts were good inhibitors of mild steel corrosion in the two different acid mediums. They all were classified as concentration dependent as their performance improved as their concentrations increased. To improve on their properties, halides were added. The Synergism improved the overall percentage inhibitor performance. Oguzie (2008a) concluded in this case that protonation of the molecules and available species which have been identified as heteroatoms were active in the corrosion retardation.

Orubite et al. (2007) explored the effect of *Nypa fruticans* wurmb extract and the blending of different concentration of KI and *Nypa fruticans* wurmb extract as corrosion retarders of mild steel in an environment of 0.1 M and 0.5 M HCl. In this work they used weight-loss methods and came up with the result that the tested coupons were more efficiently inhibited by *Nypa fruticans* wurmb in the presence of KI than pure extract of *Nypa fruticans* wurmb. They reported that a blend of the extract and KI gave the best IE% result at room temperature in 0.5 M HCl. The adsorption of inhibitor molecules aligned with Langmuir isotherm.

Synergism of polymer and iodide ion

The corrosion reduction of mild steel corrosion in 1 M concentration of sulphuric acid was investigated using polyvinyl pyrrolidone (PVP) and a blend of or synergy between PVP and iodide ions. This work was carried out using gravimetric test and the hydrogen evolution technique and reported by Umoren et al. (2009). The test was done at different temperature range from ambient temperature of 30 ^{o}C to 60 ^{o}C. The authors reported that while corrosion rates of mild steel decreased inhibition percentage performance increased with increase in the concentration of PVP. However, they observed that inhibitory property of PVP decreased as the temperature increased from 30–60 ^{o}C which as is commonly reported suggests physiosorption process of adsorption. Again, the correlation coefficient result indicates that the adsorption mechanism aligned with Freundlich and Temkin adsorption isotherms. The inhibition efficacy of PVP improved appreciably as the polymer was blended with iodide ion and as reported by the synergism parameter (S1) obtained indicate a synergistic interaction between PVP and iodide ions.

Investigation was done on four heterocyclic compounds, namely 2-amino-1,3,4-thiadiazoles (AT), 2-amino-5-methyl-1,3,4-thiadiazole (AMT), 2-amino-5-ethyl-1,3,4-thiadiazole (AET), and 2-amino-5-propyl- 1,3,4-thiadiazole (APT). These compounds were first synthesized and then used as inhibitors of mild steel corrosion in H_2S0_4 concentration of 20% at 378±2 K using weight depreciation, and Potentiodynamic Polarization at ambient temperature. Khan and Quraishi (2010) who carried out this investigation reported that the inhibition percentage performance was good and got better with the addition of potassium iodide (KI) due to synergism. While the four heterocyclic compounds were reported as good in performance, 2-amino-5-propyl -1, 3, 4-thiadiazoles (APT) was outstanding as best mild steel corrosion inhibitor. Its inhibitor efficiency was reported as approximately 87% for mild steel and 94% when blended with KI as inhibits. The adsorption isotherm test showed that the molecules obeyed Langmuir's adsorption isotherm, which implies that each active site is occupied by one molecule of the inhibitor. Potentiodynamic polarization investigations carried out at ambient temperature indicates that all the compounds studied are mixed-type inhibitors causing blocking of active sites on the metal.

Synergism of polymer, iodide ion and methionine

Oguzie et al. (2007b) examined the effect of using surface Nano crystallization as an inhibitor on low carbon steel coating (SNCLCS) that was fabricated on a low carbon steel by magnetron sputtering and the bulk steel (BLCS) as metals substrates immersed in 0.5 M sulphuric acid solution. They used EIS and Potentiodynamic polarization techniques to monitor corrosion inhibition effect of addition of methionine and the synergistic effect of adding KI. The results revealed that the two metal substrates actively corroded with no evidence of shift in passivation within the studied range of potential. They also reported that Surface Nano crystallization increased the possibility of low carbon steel corroding with reduction in the interfacial impedance and rise in the anodic reaction kinetics. While Methionine inhibited the corrosion of SNCLCS and BLCS they reported that its ability to retard corrosion enlarged with addition of KI ions due to a synergism existing between Methionine and KI ions. The effect was noticed more on BLCS than on SNCLCS.

Oguzie et al. (2007a) further examined the corrosion of mild steel immersed in sulphuric acid in the presence of Methionine (MTI) using electrochemical techniques. The effect of adding KI as inhibitor activity enhancer on the corrosion inhibition performance of the compound under study was also analyzed. MTI as seen in the result, inhibited the inhibition process. The results show that IE% improved with rise in the concentration of MTI in the corrodent solution. They also reported that upon addition of KI, the synergism increased, with an optimum result recorded when the ratio of [KI]: [MTI] was at 5:5. Authors reported that the presence of KI resulted in a stabilization of adsorbed MTI cations. The AFM surface morphological images indicate this remarkable difference. The result obtained from Potentiodynamic polarization data suggest that the compound acted as a dual type inhibitor. The fitting of the data from the temperature test carried out shows that the inhibitor aligned with Temkin adsorption isotherm. It also had a favorable compliance with Langmuir adsorption isotherm.

Synergism between compounds (used as inhibitor) and surfactant

Rafiqueea et al. (2008) used weight depreciation and Potentiodynamic polarization to study the effect of the presence of 2-aminophenyl-5-mercapto-1-oxa-3, 4-diazole (AMOD) on mild steel corrosion in a corrodent solution of HCl. They reported that AMOD sufficiently inhibited mild steel corrosion in HCl solution and recorded a good increase in its inhibition efficiency when SDS, CTAB and TX-100 surfactants were added. The analysis of their result as reported indicates that TX-100 resulted in better inhibition efficiency among the surfactants additives that were tested. The weight loss results reveal that the inhibitor percentage performance improved with rise in the surfactant concentration with a maximum inhibition efficiency recorded for maximum value of the surfactants. Furthermore, the addition of surfactant, contributed significantly to AMOD adsorption on the tested coupon surface and its conformity with Langmuir's adsorption isotherm. Rafiqueea et al. (2008) further stated that the effect of AMOD on the inhibition process is dependent on AMOD concentration, the corrodent solution temperature, and concentration of the HCl used. The effect of these parameters on the corrosion rate of the mild steel used were investigated. Their thermodynamic parameters result for the nature of the adsorption process revealed that the interaction between AMOD and the mild steel surface is good. Again they reported that while the thermodynamic studies reveal that the ΔG_{ads} values were negative implying that the adsorption process was spontaneous, the Potentiodynamic polarization results showed that AMOD inhibitor are mixed type inhibitor in the presence of the surfactants.

Water soluble polymers as inhibitors

A good number of researchers have also explored the use of water soluble polymers as inhibitors to prevent or control inhibition activities of a corrodent on a metal surface. Arukalam et al. (2014) studied the possibility of using hydroxylpropyl methylcellulose (HPMC) as a water soluble polymer to be used in retarding the corrosion of aluminium in 0.5 H_2SO_4 solution. The reported result showed that HPMC was an efficient inhibitor as it adsorbed on the metal/solution interphase. The capability of HPMC was further improved by adding iodide ions to the original stock solution. The iodide ions were supportive and had a concentrated action on the cathodic sites of the Aluminium sample surface, while the anodic sites were covered by a stable inactive oxide layer stable than the adsorption of inhibitor. They reported low values of free energy that was negative indicating a spontaneous adsorption process.

Arukalam et al. (2016) investigated two different water soluble cellulosic polymers. In the study they investigated how molecular weight affects the ability of polymers to inhibit corrosion. The metal of choice in the research was mild steel in an environment of 1 M HCl, and the polymers were hydroxyethyl cellulose (HEC) and hydroxypropyl methylcellulose (HPMC). They employed the usual technique namely gravimetric measurement, EIS and potentiodynamic polarization technique. They reported that the two cellulosic polymer inhibitors performed excellently well with a record inhibition Efficiency (IE%) of about 90%. The effect of molecular weight was observed from the result of weight loss and thermodynamic calculations to determine the best isotherm model and the later showed that HPMC with larger molecular weight adsorbed more on the corroding metal surface. Their result was further reinforced with theoretical studies results using quantum chemical calculation and molecular dynamic simulation. These results showed that HPMC molecules has superior electron donor capacity that provides electrons to fill up the vacant d-orbital of iron than the HEC molecules does.

Arukalam et al. (2014) studied corrosion inhibition potential of ethyl hydroxyethyl cellulose (EHEC) using mild steel immersed in 1 M H_2SO_4 corrodent solution. In the study they varied the concentration of EHEC and measured the loss in weight, conducted EIS and Potentiodynamic polarization. They also used quantum chemical calculation method. They reported that EHEC is a good corrosion inhibitor with an increased IE% as its concentration in the corrodent solution increased. Here again the influence of iodide ions was observed and its synergistic effect proved positive. The EIS result confirmed an adsorption of the molecules of EHEC on the metal surface immersed in the corrodent solution. The free energy of adsorption (ΔG_{ads}) values were reported as negative and fitted well into modified Langmuir isotherm. Also the Potentiodynamic Polarization result shows that EHEC is a mixed type inhibitor with a leaning towards cathodic partial reaction. A theoretical analysis of the results in other to characterize the adsorption of the inhibitor at molecular level using density functional theory that examined the frontier molecular orbitals, (HOMO and LUMO) and the local reactivity of the inhibitor molecules agreed with the results got from laboratory experiments.

Solomon et al. (2010) investigated the inhibitive and adsorption effect and actions of carboxymethyl cellulose (CMC) on Mild Steel corrosion when its coupons are immersed in Sulphuric acid solution. This study revealed that when the concentration of CMC increased there was an associated increase in the inhibition efficiency of the polymer while increased temperature reduced its IE%. They used activation parameter data to substantiate the weight loss measure. The effects of poly(vinyl alcohol) (PVA), poly(acrylic acid) (PAA), sodium polyacrylate (NaPA), poly(ethylene glycol) (PEG), pectin (P), and carboxymethyl cellulose (CMC) as corrosion inhibitor of the corrosion of cadmium in half of 1M hydrochloric acid (HCl) solution were studied more than a decade ago by Khairou and Elsayed (2003). Both electrochemical impedance spectroscopy and Tafel plot techniques. Cathodic and anodic measurements were carried and the study showed that all the polymers inhibited effects on both the cathodic and anodic processes except for NaPA, P, and CMC which did not have much cathodic effect at lower concentrations. They explained this behavior likely to be as a result of very weak adsorbability of the polymers on the cathodic sites. Again they suggested that because of the hydroxy groups in PVA and PEG, the polymers (PVA and PEG) bridged the HCl solution action on the metal surface even though according to them PVA had better adsorbability on the surface than PEG at the anodic potential. They concluded that the adsorption behavior of the polymers obeyed Temkin adsorption isotherm.

Processes employed by researchers for extraction of plant extracts for corrosion test

The extraction process for compounds in plants takes different forms based on the desired quality of the extract sort after. Amita and Shalini (2014) reported that the techniques of extraction include but are not limited to hot Soxhlet otherwise known as continuous extraction, aqueous – alcoholic extraction, microwave-assisted extraction, distillation technique and phytonic extraction. Some other extraction methods come handy for extraction of aromatics and they include – headspace trapping, solid phase micro extraction and micro distillation. While the quality of the extract is dependent on the part of plant used, the extraction procedure and solvent used, the effect of extraction of the phytochemical compounds depend on the nature and type of plant, moisture content, particle size and the degree of processing involved. They also stated that parameters that affect the amount of extracts derived depend on the type of extraction, extraction time and temperature. The type of solvent used, its concentration and polarity, also contribute to the quantity of extract obtained, while the active components can be derived from any part of the plant used for the extraction.

The choice of solvent depends on the active compounds to be extracted and the use. So this implies that for extracts from plant material to be used for corrosion control it is largely dependent on the type of solvent used in the extraction procedure. Amita and Shalini also reported that the desired properties of a good solvent in plant extraction process include, Low toxicity, Ease of evaporation at low heat, Promotion of rapid physiologic absorption of the extract, Preservative action and inability to cause the extract to complex or dissociate. They isolated a number of factors that affect the choice of solvent and they are, Quantity of phytochemical to be extracted from the plant, Rate of extraction, Variety of different compounds extracted, Diversity of inhibitory compounds extracted, Ease of subsequent handling of the extracts, Toxicity of the solvent in the bioassay process, and Potential health hazard of the extracting medium. Overall, the choice of a solvent is influenced by what the desired aim and objective sort after upon getting the extract. Since the end product will contain traces of residual solvent, the solvent should be nontoxic and should not interfere with the bioassay. The choice will also depend on the targeted compounds to be extracted.

The differences in the extraction methods employed will usually depend on, Length of the extraction period, Solvent used, pH of the solvent, temperature, particle size of the plant tissues and the solvent-to-sample ratio. The basic principle is to grind the plant material (dry or wet) finer, which increases the surface area for extraction thereby increasing the rate of extraction. Earlier studies reported that solvent to sample ratio of 10:1 (v/w) solvent to dry weight ratio has been used as ideal. The basic solvents that have been used for active component extraction are: Water, Ethanol, Methanol, Chloroform, Ether and Acetone. For corrosion extraction test, researchers have used the acid to be used as the corrodent solution such as HCl, H_2SO_4 and any other acid desire for the corrosion test.

Oguzie (2008b) reported that the Stock solutions used in the reported research work were prepared by weighing out an amount of the ground plant and having it boiled in the acid to be used for the corrosion test–2 M HCl and 1 M H_2SO_4, for 3 h. The solutions were allowed to get cooled and then filtered and stored. The measured weight of the dried residue was subtracted from the initial weighed grounded plants. Using acid as the solvent, the filtrate which is the inhibitor test solutions were then prepared to have corrodent solutions having concentration range 10–50 v/v% of the inhibitors.

Later, Oguzie et al. (2010) carried out the extraction process of the plant by having weighing dried and ground leaves of Dacryodis edulis refluxed for a total of 3 h in 1 M Hydrochloric acid and 0.5 M sulphuric acid solutions, respectively. The solutions resulting from the reflux process were allowed to cool after which they were filtered thrice and the quantity of the plant content extracted was calculated by subtracting the weight of the dried residue with the weight of the initial dried plant material before the extraction was carried out. The Dacryodis edulis inhibitor based solutions to be used for the test were prepared to give the concentration range of 5–1000 mg/L.

Al-Otaibi et al. (2014) collected five hundred gram aerial parts of *L. shawii* (L.S.), *T. oliverianum* (T.O.), *O. baccatus* (O.B.), *A. garcinii* (A.G.), *C. italica* (C.I.), *A. sieberi* (A.S.), *C. tinctorius* (C.T.) and *T. auriculatum* (T.A.) plants and dried them in a shade and then grind them to powdered form defatted them thrice at room temperature for 72 h respectively using petroleum ether at 60–80 °C. after which the plants extracted using chloroform and then finally with 95% ethanol three times at room temperature for 72 h each. The combined alcoholic extracts of each plant were concentrated under vacuum at 40 °C until solvents were completely removed. These dried alcoholic extracts of each plant were used for corrosion inhibition activity tests.

Fouda et al. (2017) investigated *Tilia cordata* plant leaves. The leaves were dried in air, grinded to powdered form and 150 g of the pulverized leaves was dissolved in 250 ml of double distilled H_2O, boiled for 30 min, allowed to cool in place devoid of sun light. The resulting crude extract was filtered to remove unwanted solid remainders and contaminants. 10 ml of the crude extract was desiccated at fixed temperature and the resulting solid residue was weighed to establish the concentration of the aqueous extract. To prepare a stock solution of 1000 mgL^{-1} required, 70 ml of the crude extract was taken and completed to 1000 ml with double distilled water.

In another report, Sappani and Sambantham (2013) prepared stock solutions of the crude extract of torsemide and furosemide by refluxing 40 g of the dried and grinded leaves in 500 ml absolute ethanol for three hours. The amount of the plant extracts extracted into solution was calculated by subtracting the weight of the dried residue from the initial weight of the dried plant material before extraction. Inhibitor test solutions were prepared in the concentration range 50-1200 mgL^{-1} from the stock solution.

Al-Senani and Alshabanat (2018) in a study of the corrosion inhibition of carbon steel in 1 M HCl using extracts of Date Palm waste extracted the extracts after treatment of the date wastes by missing 2 g of the dried powdered Date Palm with 200 ml of 1 M HCl and then refluxed at 50 °C for 2 hours. The extracts were cooled and filtered using Whatman filter paper and the filtrate was kept as stock solution from which test solutions of different concentrations were prepared. Pedroza-Periñán et al. (2016) carried out an extraction of Theobroma Cacao pod husk using 96% v/v ethanol. 50 g of the undried cacoa pod with 84 % w/w moisture content was milled and added to 300 ml of the solvent at a constant temperature and specific and solution was filtered and stored for corrosion test.

Identified knowledge gap

As seen above from the review although water as a universal solvent can be used for extraction not so much of it has been used. It is therefore the interest of this authors to research the extraction of plant extracts using water at ambient temperature. Also, there has been blending of different forms of inhibitors with halides and surfactants with minimal investigation into blending of cold water crude extracts of plants and water soluble polymer. This rear blend demands investigation to explore inherent opportunities and possibilities for corrosion inhibition (El-Lateef and Elrouby, 2020; El Aoufir et al., 2020; Emori et al., 2020; Fu et al., 2020; Guruprasad et al., 2020; Joz Majidi et al., 2020; Khan et al., 2020; Pourfarzad et al., 2020; Singh et al., 2020; Yuan et al., 2020).

CONCLUSIONS

It is anticipated that the inhibitors produced from the extracts of plants can be blended with water soluble polymers to derive cheap inhibitors that will be easy to produce and with easy applicability in the field. Products got from blending polymers and the crude plant extracts will progress the search for natural replacement for toxic and expensive inhibitors. It is also expected that the mechanism for the new inhibitor adsorption on metal surface can be elucidated following existing models.

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