An Overview of Corrosion Inhibition using Green and Drug Inhibitors

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Abstract.
Corrosion has been a predominant problem for industries ranging from oil and gas to automobile. Various methods have been utilized to combat this phenomenon, some methods have causes great environmental effect that are harmful to humans. This has necessitated the use of green corrosion inhibitors. This review paper delves into the subject matter and reports the inhibition efficiency of green corrosion inhibitors that have been used for combating corrosion, because of their eco-friendly nature.

Keywords: Corrosion, Green corrosion inhibitors, Industries.

1. Introduction
Corrosion is the damaging occurrence of metals by reacting with its environment and a natural latent threat accompanying with oil and gas industries [1]. Most corrosion agents or triggers are oils, water, liquid chemicals, gaseous materials and humidity in the air [2]. Corrosion of aluminium shows a detrimental effect like reduce chemical reactivity of cathode active components, taints the electrolyte, electrical resistance and intensify the self-discharge rate [3]. Oil and gas industries have suffered severely from corrosion, oil pipeline rupture, chemical leakage and even fire. This is caused by the recurrent extraction of free water and highly corrosive media: like H₂S and CO₂ running through oil and gas machines, causing a total annual cost estimated to $1.372 billion [1, 4]. Various categories of corrosions are selective leaching, galvanic corrosion, crevice corrosion, intergranular corrosion, pitting corrosion, erosion corrosion, and uniform corrosion. Uniform corrosion leads to gradual loss in the surface thickness of the metal or material uniformly. It is effortlessly expectable, and this diminishes the degree of failure of materials. Aluminium controls this causes of corrosion by its protective oxide layer on its surface [5]. Crevice corrosion occurs in the opening or crevice on the surface of metals, which narrow for either acidic or alkaline solutions to breach and get stuck in it. This tends to lessen the cathodic reactions in that region and giving an overall anodic characteristic. Due to the disparity of the cathodic and anodic effects, the crevice regions become highly corrosive and lead to the material decomposition [6]. Pitting corrosion occurs on the metal surface, forming small holes. Pitting corrosion is barely detected, until failure of the material. This makes it, the most hazardous form of corrosion. It happens on passivated materials and alloys in specific environments comprising of iodide, chloride ions and when the electrode potential surpasses a dangerous value [7]. Intergranular corrosion includes enhanced rust or disintegration laterally the grain boundaries of any material, although the material surface is not rusted. Intergranular corrosion attacks the microstructural grains of the material, leading to lessen toughness, cannot withstand some tensile stress and can fracture without notice. It can be caused, due to galvanic elements [8]. Corrosion that happens between two different metals in contact with each other either indirectly or directly is galvanic corrosion. It can also happen between other conducting materials like graphite, metals and alloys [9]. Corrosion is the reduction of metals due to cathodic and anodic chemical reactions between metals and their surrounding environments. Cathodic chemical reactions are due to the decline of oxygen or the raise of hydrogen by an element, in an acidic environment, as shown in Equation 1. Cathodic chemical reactions are present in the deoxidizing or desmut operation [10]. While, anodic chemical reaction occurs due to oxidation. Oxidation is the reduction of electrons, the increase of oxygen or the decline of hydrogen by any element. This reaction is accountable for the actual depletion of the mass of any material or metal corroding [5].
O_2 + 4H^+ + 4e^- → H_2O (aq) \quad (1)

Corrosion exists in two forms: dry and wet corrosion. Dry corrosion can be well-defined as; material decomposition that occurs with the interaction of metals with oxygen in the air, which outcomes is the formation of oxide layer-rust on the surface of the metals. This oxide layer-rust stops the continuous decomposition of the metal and this phenomenon is called passivation. While, wet corrosion is defined as material deterioration that occurs in an aqueous solution of water, acid or alkali [10]. Corrosion cannot be practically eradicated but can be controlled or inhibited to a certain degree. There are numerous methods to protect from and control corrosion. The two main ones are inhibition of surface corrosion and protective coatings. Inhibition of surface corrosion is carried out by using chemical inhibitors or organic inhibitors to control various factors that enhance the cause of corrosion. While protective coatings, is achieved by painting the surface of the material, electroplating, electroless plating of the surface, galvanizing and many more. Other methods to control corrosion are modification of the metal(alloying), prevention of surface reactions (cathodic and anodic protection methods), modification of surface conditions e.g. designing oil pipes to control or prevent crevices [11]. Inhibition of surface corrosion is the most economical method or method to mitigate corrosion [12]. Corrosion inhibition is being utilized in numerous industries or industrial applications, to protect pipes in oil and gas sector, to inhibit or control the decomposition rate of boilers, feed-water sections and to reduce sulphide-induced decomposition in industries used for gasification or steel pipelines. Which is often induced by the presence of dissolved acidic oxides or oxygen. Since corrosion is a surface reaction, therefore it suggests that it can be inhibited or controlled by the introduction of external inhibitors on the surface. Corrosion can also be caused, by the speed of the fluid in the pipes [1]. Corrosion can also be caused in industries, due to the utilization of acids, which is used for cleaning, picking and descaling [13].

In searching for various solutions to reduce the effect of corrosion and replacement for inorganic corrosion inhibitors, surface treatment using green corrosion inhibitors has become a rewarding alternative. Inorganic corrosion inhibitors like chromate, dichromate, nitrite and nitrate, especially chromate, biotoxicity have been documented and most industries have started outing to alternative effective eco-friendly corrosion inhibitors and most are interested into the utilization of green corrosion inhibitors; plant extracts have become acceptable due its availability, than drug corrosion inhibitors [14]. The use of green eco-friendly natural polymeric structures is having a large preference, due to its practical use, renewable sources of materials, low cost and safe effect and can also be easily extracted from leaves or seeds [15]. Drug inhibitors are inorganic green inhibitors [11]. [16] carried out an analysis on inhibition of the gradual deterioration of materials, using expired carbamazepine and paracetamol tablets, it was obtained that for carbamazepine, the decomposition carbon steel weathering inhibition in 0.1 mol L\(^{-1}\) H\(_2\)SO\(_4\) was around ninety percent, while for paracetamol, the decomposition inhibition effectiveness of carbon steel in the 0.25 mol L\(^{-1}\) acetic acid–0.25 mol L\(^{-1}\) sodium acetate buffer solution was around eighty-five percent. This shows the potential of use of drugs as material deterioration inhibitors. [17] stated the inhibitory action of penicillin because of their physical adsorption on the surface of mild steel, which is due to weak intermolecular interactions. [18] itemised that, many successful researches on corrosion inhibition have been carried out using natural products like lignin terpolymer, phyllanthus amarus extract, aqueous extract of opuncia plant stem, azadirachta indica leaves extract, cassava starches and this natural corrosion inhibitors were successfully as rust inhibitors for aluminium. Gums, natural oils and antibacterial drugs can also be considered as green inhibitors. Green inhibitors provide a new, less costly and environmentally friendly method to reduce corrosion. According to [4] figure 1 shows the research work distribution in the last two decades on the various sector shown in figure 1. It reveals that most of publications are focused on the study of plant extracts.
Figure 1. The distribution of the research work done on natural products as corrosion inhibitors. [4]

An effort to discover rust inhibitors that are eco-friendly or environmentally harmless, easily accessible and obtainable; has showed an increase of interest in the utilization of natural products called green corrosion inhibitors, which are extracts of leaves or plants used as rust inhibitors for metals in acid-cleaning process. Plant extracts of Nypa fruticans, opuntia plant stem, Azaricta indica, Ocimum viridis, Phyllanthus amarus, Zenthoxylum alatum, lignin terpolymer, spondias mombin, cassava starches and Chamomile have been tested as corrosion inhibitors [15, 18].

2. Green Inhibitors

[19] studied the corrosion inhibitive efficiency of two derivatives (BHC and PHC) of chitosan oligosaccharide on P110 steel. At 80 °C the inhibitive efficiency of the two chitosan derivatives on the steel was analysed by utilizing potentiodynamic polarization method, gravimetric method, and the surface morphology of the steel was characterized by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The inhibitors successfully adsorbed on the surface of the substrate. Simulated saline medium was used as the corrosion testing medium. The corrosion test via electrochemical impedance showed that the inhibitor offered high degree of corrosion resistance.

[20] studied the properties of synthesized polysaccharide esters (KGMH and KGMA) which were used as rust inhibitors, where a modification of Konjac glucomannan (KGM) utilizing amino acids. It was found that the synthetic polymers had a lesser water absorbency and a better water solubility than KGM. Utilizing gravimetric measurements, it was shown that highest efficiencies of KGMH and KGMA for lessening the rust rate of metal at 2000 ppm are up to 92.4 percent and 89.9 percent, respectively. SEM and EIS were utilized. The SEM analysis proposed an effective decomposition inhibition of the steel in HCl. While the polarization curves showed that the inhibitory effect and that the metal dissolution reaction was dependent on the change in the concentration.

[21] studied two synthesized pyridazinium-based ionic liquids, their inhibitive efficiency was examined utilizing electrochemical impedance spectroscopy (EIS) at a temperature range of (303–333K). Mild steel was inhibited in 1 M HCL, using the synthesized pyridazinium-based ionic liquids. The synthesized liquids viz. 1-(2-bromoacetyl) pyridazinium bromide (S2) and 1-(6-ethoxy-6-oxohexyl) pyridazin-1-iium bromide (S1) showed that with a surge in their concentrations, there was efficiency rise to 82 percent and 84 percent respectively at 303K, an upsurge in the charge transfer resistance (Rct) and a decline in the double layer capacitance (Cdl). Also, the sign of free energy (ΔG_ads) values, showed a proportional rise with temperature, while using the inhibitors.
[22] investigated the inhibitive efficiency of utilizing pyrazine derivatives ((Pyrazine C) 2,3-pyrazine dicarboxylic acid as a green corrosion inhibitor, in 15 percent HCl. Their inhibition on X60 steel were inspected, using electrochemical frequency modulation (EFM), linear polarization resistance (LPR) at 25 °C, electrochemical impedance spectroscopy (EIS), gravimetric analysis at 60 °C and 90 °C for six hours and potentiodynamic analysis. The results gotten presented that the efficiencies of pyrazines E and C at 60 °C, remained unchanged regardless of the rise in their concentrations, although at 90 °C the efficiency of pyrazine E amplified with concentration while pyrazine C stayed constant. Pyrazine H inhibitive efficiency at 60 °C and 90 °C increased with concentration. Inhibition effectiveness of pyrazine E and C was improved by adding Glutathione (Glu) and sodium Iodide (NaI) but it had no substantial effect on pyrazine H. It was found that the pyrazine derivatives were mixed -typed inhibitors, while utilizing the potentiodynamic study. The surface morphology of X60 steel was also examined.

3. Various Application and Properties of Extracts from Plants

[23] examined the latent ability of the alkaloidic extract of Xylopia cayennensis as a corrosion inhibitor of C38 steel in 1M HCl. The extract was studied utilizing electrochemical impedance spectroscopy and potentiodynamic analysis. It was discovered that, the extracts had an efficiency up to 93 percent and 94 percent respectively for 200 mg/L and the extract acts as mixed inhibitor as indicated, by the methods utilized. The effects of temperature, time immersion and adsorption mechanism were discussed.

[24] studied the corrosion inhibition properties while combining Urtica Dioica (UrDi) and praseodymium nitrate (PrN) on mild steel in sodium chloride mixture. Further examination like Fourier transform infrared (FT-IR), thermogravimetric analysis/differential thermogravimetry (TGA/DTG), ultraviolet-visible (UV-Vis) and X-ray photoelectron spectroscopy (XPS) established the compound development between UrDi (Pr-UrDi) and Pr cations. 94 percent decomposition inhibition using Pr-UrDi hybrid complex on the steel, was revealed from the electrochemical results.

[25] studied the inhibition effect happening during the weathering of heat exchanger tubing material (titanium tubes) in MSF desalination plants using aromatic nitro compounds in acid cleaning solution (1.0M H2SO4). Further investigation on the surface morphology of titanium was carried utilizing FTIR and SEM analysis. The results showed that aromatic nitro compounds performed as an active rust inhibitor for titanium in acid cleaning solution. It also showed, the highest deterioration degree of titanium (0.260 mgcm⁻² h⁻¹) was attained in 1.0M H2SO₄ at 298K between electrochemical (EIS) and chemical methods being reported. The efficiency of these compounds surges with concentration and reduces with temperature.

[26] studied (EEMAS) ethyl acetate extract from mature arecanut seed and (WEMAS) water extract from mature arecanut seed as a rust inhibition on aluminium in 0.5 M HCl. This analysis was seriously analysed by the utilization of surface morphology study (SEM and AFM) techniques, gravimetric method and electrochemical (Tafel plot and AC impedance). From the Tafel plot analysis, the material decomposition current value declines significantly with an upsurge in the plant product concentration. The gravimetric method showed that this rust control was at its peak at the concentration of 12 gl⁻¹ of plant extracts. AC impedance spectroscopy method displayed that an upsurge in the charge transfer resistance values with the accumulation of plant extract elements to the wear away of the medium. Surface morphology characterisation of the target metal by the utilization of (SEM) scanning electron microscopy and (AFM) the atomic force microscopy, gave prominent hint about the defensive part of plant extracts on the substrate utilized.

[27] examined the inhibition behaviour mild steel at numerous concentrations and temperatures, in 0.1 M HCl utilizing spondias mombin leaf extracts. The outcome discovered that the inhibition efficiency of the extract on the mild steel sheet improved with cumulative concentration of the extract and declined with surge in temperature. Adsorption isotherm proved to follow Freundlich adsorption isotherm.

[28] studied the inhibitive efficiency of spondias mombin leaf extract aluminium in 0.5 M H2SO4. Gravimetric method examined, the inhibitive efficiency of spondias mombin leaf extract at temperature between 30°C to 60 °C. The results showed that, spondias mombin leaf extract was an effective rust inhibitor for aluminium. There was an upsurge in the inhibition efficiency of spondias
mombin leaf extract with an increase in its concentration, but it declined with temperature. Addition of potassium iodide increased the inhibition efficiency. Spondias mombin leaf extract adsorption proved to follow Langmuir adsorption isotherm.

[29] studied the corrosion inhibition of 304 stainless steel, utilizing Salvia officinalis (S. officinalis) leaf extract in 1M HCl by means of potentiodynamic analysis, electrochemical impedance spectroscopy (EIS) and gravimetric measurements. Tafel polarization analysis discovered the extract of Salvia officinalis leaf extract acted as a mixed type inhibitor. Salvia officinalis leaf extract adsorption proved to follow Langmuir adsorption isotherm. Quantum chemical calculations utilized the semi-empirical method (AM1) and (DFT) density functional theory to exemplify the procedure of adsorption of Salvia officinalis leaf extract.

4. Inhibitive Effects of Drug Inhibitors

The corrosion resistance of mild steel was investigated in 1 M HCl by [12] using Streptomycin. The analysis was examined by weight loss measurement, Tafel polarization, and electrochemical impedance spectroscopy (EIS). Streptomycin exhibited 88.5 percent inhibition efficiency at 500 ppm concentration. Inhibition occurs due to the adsorption of the drug on metal surface, altering the deterioration process. Polarization analysis recommends Streptomycin as a mixed type of inhibitor. Electrochemical impedance spectroscopy method was also utilized to inspect the rust inhibition.

[30] analysed the inhibitive efficiency of Pheniramine drug on mild steel corrosion in 1 M HCl solution examined utilizing gravimetric analysis, linear polarization resistance, electrochemical impedance spectroscopy and potentiodynamic polarization measurements. Adsorption process follows the Langmuir adsorption isotherm. The values of activation energy (Ea) and different thermodynamic parameters such as adsorption entropy (S_ads), adsorption enthalpy (H_ads), free energy of adsorption (G_ads), and adsorption equilibrium constant (K_ads) were considered and debated. The adsorption process of examined drug on the steel surface complies that pheniramine mixed-type inhibitor.

[31] investigated the utilization of four compounds of antibacterial drug as corrosion inhibitors on aluminium in 2M HCl solution. The study was done with gravimetric analysis, hydrogen evolution and potentiostatic analysis. While the polarization curves showed that the inhibitory effect and that the metal dissolution reaction was dependent on the change in the concentration. Adsorption process follow Langmuir adsorption isotherm.

5. Conclusions

From the inclusive review carried out, it was observed that green corrosion inhibitors are effective and eco-friendly. They reduce the weight loss with increase in their concentration as acknowledged by scholars. Corrosion is very destructive to life of materials, especially those used at industries. Various techniques like inhibition of surface corrosion, protective coatings, modification of the metal(alloying), prevention of surface reactions (cathodic and anodic protection methods), modification of surface conditions (e.g. designing oil pipes to control or prevent crevices) have been used to prevent or control the weathering effect. In inhibition of surface corrosion, chemical or inorganic compounds have been used, but have hazardous effects on the environment. The need for green corrosion inhibitors is very essential.

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