Review

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Organic green corrosion inhibitors (OGCIs): a critical review

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Abstract: Over the decades, corrosion has resulted in loss of lives accorded with damage costs in almost all engineering fields. Thus, it is seen as an environmental threat with catastrophic attributes, which calls for day-to-day research on its final resolution. Recent studies have proven organic green corrosion inhibitors (OGCIs) from plant extracts with biodegradable, environmentally accommodative, relatively cheap, and nonharmful features as the most perfect approach of tackling the problem. This review gives succinct discussion on the mechanisms, classifications, and active functional groups of OGCIs. Measuring ways and factors influencing their efficiency are presented. Also, various plant extracts used as OGCIs in preventing material corrosion in corrosive media coupled with their respective findings, applied characterization techniques, and future challenges are presented. The significance of values obtained from simulating presented mathematical models governing OGCI kinetics, adsorption isotherm, and adsorption thermodynamics is also included. In conclusion, recommendations that will broaden the usage of OGCIs from plant extracts for inhibiting corrosion of materials are presented for prospective researchers in the field of corrosion.

Keywords: corrosion; corrosive media; green; inhibitors; organic.

1 Introduction

Corrosion is metal degradation as a result of contact with aqueous corrosive surroundings (air, moisture, or soil; Thompson et al., 2007) through direct chemical or electrochemical reaction to form noble compounds (Uhlig, 1971).

As defined by the International Union of Pure and Applied Chemistry, corrosion is an interfacial material (polymer, metal, concrete, wood, and ceramic) reaction (irreversible) with its environment, which results in material consumption or in dissolution into the material of an environmental component (Vadivu et al., 2016). Corrosion is an environmental threat with economic, conservation, and safety impacts in various engineering applications such as building construction, chemical, automobile, mechatronics, metallurgical, and medical (Sharma et al., 2011). Various forms of material corrosion under different environments have been discussed (Popoola et al., 2013). Thus, there is a need to develop novel techniques and methods of tackling this dangerous phenomenon from existing prominent ones, which are protective coatings and linings, cathodic/anodic protection, and corrosion inhibitors. However, the results of numerous research conducted in anticorrosion material applications in previously mentioned engineering fields revealed using corrosion inhibitors as the most effective and simple approach of preventing deleterious degradation of metals and alloys in corrosive media (Basargin et al., 2004; Singh, 2014). Figure 1 depicts the summary of chemical reactions of the corrosion process.

Corrosion inhibitors minimize or avert corrosion when added in small concentrations to a corrosive medium (Riggs, 1973) by forming monomolecular film-adsorbed surface (Mainier et al., 2003), which obstructs the direct contact between metal and corrosive agents (Ebenso et al., 2012). They have been classified based on sources (as organic or inorganic) and techniques (as synthesized or extracted). Thus, it is required to look for not only applicable corrosion inhibitors but also those that are economically viable and environmentally friendly. However, synthetic organic corrosion inhibitors (SOCIs) and traditional inorganic corrosion inhibitors (TICIs) such as chromates and lead have been known to have restrictive environmental regulations (Raja and Sethuraman, 2008) due to their hazardous effects. Many of the SOCIs are not biodegradable and get accumulated in the environment constituting nuisance to human health or ecological systems (EPA, 1998), the removal of which is complicated

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Figure 1: Chemical reactions of the corrosion process (Brylee and Advincula, 2015).

and expensive (Bammou et al., 2011). These environmental issues have called for a replacement of these TICIs and SOCIs with natural organic compounds sourced from spices, naturally existing aromatic herbs, and medicinal plants that can hinder the corrosion of materials in corrosive media called organic green corrosion inhibitors (OGCIs), which are inexpensive, harmless, readily obtainable, and environmentally accommodative. Figure 2 presents the various sources of eco-friendly OGCIs.

Historically, the use of OGCI started in the early 1930s when extracts from plants such as *Chelidonium majus* (celandine) are first used for sulfuric acid (H_2SO_4) pickling baths (Sanyal, 1981). Thereafter, researchers around the world found interest in using green anticorrosive agents extracted from several natural plants (Schmitt et al., 2009). Seeds, fruits, leaves, and flowers of natural plants such as *Justicia gendarussa* plant extract (Satapathy et al., 2009), khillar (El-Etre, 2006), olive leaves (El-Etre, 2007), *Phyllanthus amarus* (Okafor et al., 2008), and *Murraya koenigii* leaves (Quraishi et al., 2010) have been extracted and applied as corrosion inhibitors. Results revealed natural plants extracts to be easily obtainable, biodegradable, and harmless (Ji et al., 2015) with remarkable potential of inhibiting corrosion reaction.

1.1 Mechanisms of OGCI

The corrosion inhibition efficiency of OGCI has been linked to the availability of organic compounds with N, O, P, and S atoms (Yildirim and Cetin, 2008), which have shielding effect and corrosion-inhibiting potentials for material attack. Their increasing order of corrosion inhibition efficiency has been stated to be oxygen < nitrogen < sulfur < phosphorus (Neha et al., 2013). OGCI exhibit their inhibiting action via physisorption or chemisorption

Figure 2: Sources of eco-friendly OGCI (Ibrahimi et al., 2017).

onto the metal-solution interface by removing molecules of water on the surface for compact barrier film formation (Finšgar and Jackson, 2014). The occurrence of a coordinate covalent bond by interaction between lone pair and π -electrons available in the molecules of OGCI with the vacant metal d -orbitals is also experienced (Abdallah, 2002). Nevertheless, compound adsorption on the metal surface is enhanced by p - d bond formation as a result of p -electron overlap to the $3d$ vacant orbital of Fe atom (Ahamad et al., 2010) due to the availability of N, O, and S atoms and organic structure double bonds (Hong et al., 2008).

Generally, adsorption types can be distinguished by the occurring mechanisms that can be physisorption, chemisorption, interaction between metal and p -electrons, or mixture of the aforementioned (Tian et al., 2012). The chemical structures of OGCI, inhibitor molecule charge distribution, and metal surface charge determine the process of adsorption. In physisorption, electrostatic attractive force binds ionic charges on OGCI molecules with electric charged metal surface, whereas chemisorption occurs via sharing of free electron pairs or transfer of charge to produce strong chemical bonds between non-ionic OGCI molecules and the metal (Papavinasam et al., 2007). However, the chemisorption bond strength is a function of the functional group electron density present on the donor atom and group polarizability. OGCI inhibition efficiency is improved when one of the H atoms attached to the C in the heterocyclic ring is displaced by any of -CHO, -NO, -COOH, or -NH₂ substituent group (Ali et al., 2003). Also, cathodic or anodic reactions are being retarded when metal electron density changes at the point of attachment. The consumption of electrons at the cathode occurs while they are furnished at the anode (Kartsonakis et al., 2012).

1.2 Classifications of OGCI

Corrosion inhibitors from greeners can be either scavengers or interface inhibitors. Scavengers reduce medium corrosivity by scavenging aggressive substances, whereas interface inhibitors inhibit corrosion through film formation at the metal-environment interface. Scavengers work in alkaline and almost neutral solutions by cathodic-oxygen reduction reaction simply written as Eq. (1). The interface inhibitors are classified as either vapor phase or liquid phase. The vapor-phase inhibitors provide temporal atmospheric corrosion protection especially in closed environments by loosely impregnating wrapping paper inside a closed container (Levin et al., 1965). The OGCI

transport and metal surface interaction occur during the vapor-phase inhibition process.

However, the most prominent are the liquid-phase inhibitors that are further subdivided into cathodic, anodic, or mixed OGCI based on the reaction-type inhibition, which can be any of the cathodic, anodic, or both electrochemical reactions. In anodic OGCI, hydroxides, oxides, or salts are produced to enhance passivating film formation, which inhibits anodic metal dissolution reaction. Their mechanism is best explained by an active-passive metal polarization diagram. In cathodic OGCI, corrosion is controlled by either cathodic poisoning or cathodic precipitation. In the former, sulfides and selenides, which act as cathodic poisons, are adsorbed on the surface of the metal to form protective films that reduce the rate of cathodic reaction through oxygen diffusion minimization on the metal surface. In the latter, insoluble compounds such as carbonates of calcium and magnesium are precipitated on the metal surface to increase alkalinity at cathodic sites. Generally, hydrogen ion reduction to H atoms to form molecules of hydrogen as written in Eqs. (2) and (3) occurs in acidic solution, whereas cathodic reaction occurs via the reduction of oxygen in alkaline solution.

Lastly, approximately 80% of OGCI are categorized as mixed inhibitors that protect the metal from corrosion by chemisorption, physisorption, and film formation. Physisorption is facilitated by the electrostatic attraction of negatively charged (anionic) OGCI with positively charged metal surface. Chemisorption process is slower than physisorption such that the inhibition rate and adsorption increase as the temperature increases (Sastri, 2011). Corrosion protection also increases with the increase in polymeric films produced as a result of OGCI molecules adsorbed, which are subjected to reactions on the metal surface. Insoluble adherent films that avert solution access to the metal provide effective inhibition.

1.3 Active functional groups in OGCI

The OGCI active ingredients consist of phytochemical constituents known to be functional groups with N, O, S,

P, or Se heteroatoms via which they are attached onto the metal surface (Helen et al., 2014). Compounds of OGCI with abundant *p*-electron and functional electronegative groups with conjugated double or triple bonds have been shown to be most effective (Jiang et al., 2007). The inhibitor molecule efficiency to cover enough surface area is increased due to the attached groups to the parent chain. In lieu of this, the bonding strength of the group on the metal is enhanced by the presence of peculiar repeating units (methyl and phenyl groups) of the parent chain and additional substituent groups. Studies have shown that OGCI molecules with -OH and -OCH₃ electron-releasing substituents proved to have better efficiency than the parent molecule with no substituents (Verma et al., 2017). Also, heterocyclic compounds have exhibited higher corrosion inhibition efficiency, as they attach easily on the metal surface via their π - and nonbonding electrons, aromatic rings, and polar functional groups that act as adsorption centers (Ahmad et al., 2010). Table 1 presents some anchoring functional groups present in OGCI.

Some prominent compounds such as benzoic acid (Akiyama and Nobe, 1970), benzotriazole (Fox et al., 1979), thiourea (Singh, 1993), flavonoids (Bhola et al., 2013), carbohydrates (Umoren and Eduok, 2016), tannins (Nonaka, 1989), and tryptamine (Suleiman et al., 2013) containing these active functional groups whose sources are from natural plants have been applied as corrosion inhibitors for many metals. Flavin mononucleotide from grape pomace extracts has been detected as a good OGCI for hot-rolled steel in acidic medium (Bhola et al., 2013). Its corrosion inhibition potential lies in the presence of heterocyclic isoalloxazine ring anchored to sugar alcohol-ribitol obtained from D(-) pentose sugar (ribose), which consists of a phosphate monosodium salt and three antisymmetric carbons. The bark of *Rhizophora racemosa* stem investigated to be very rich in tannins has been stated as the most effective OGCI for mild steel. Its

basic structure contains residues of garlic acid attached to glucose through glycosidic bonds (Nonaka, 1989) with arrays of hydroxyl and carboxyl groups enhancing molecule adsorption on corroding mild steel surfaces. *Chamaerops humilis* plant extract, which is also rich in tannins, is effective in inhibiting corrosion of mild steel in 0.5 M H₂SO₄ with 5% ethanol additive (Benali et al., 2013). Tryptamine, a derivative of the tryptophan, proved effective in inhibiting ARMCO iron corrosion in deaerated 0.5 M H₂SO₄ within a temperature range of 25°C–55°C. Table 2 presents the various sources of OGCI with their respective functional groups and inhibitory roles.

1.4 Factors influencing OGCI efficiency

OGCI efficiency in inhibiting corrosion is a function of their adsorption characteristics on the metal surface. Factors that have been considered by previous studies affecting OGCI inhibition efficiency depend majorly on their structure, concentration, temperature, and exposure time. An increase in OGCI concentration results in a simultaneous decrease in corrosion rate with an increase in inhibition efficiency, which approaches optimum level at a certain concentration value. This resulted from the formation of additional inhibitor molecules being adsorbed on the surface of the metal, which makes it complex for further corrosive attack to occur by the electrolyte solution. The dissolution of metal increases with corrosion exposure period in the presence of OGCI. This is linked to previously adsorbed inhibitor molecules from the metal surface resulting from partial desorption. Corrosion rate increases linearly as temperature increases such that an equilibrium exists between adsorption and OGCI molecule desorption at the surface of the metal at a particular temperature. An increase in temperature as a result of a higher desorption rate makes the equilibrium to shift until its reestablishment at various equilibrium constant values. Thus, OGCI inhibitive protectiveness decreases with increasing temperature. As mentioned previously, OGCI structural behavior has a great influence on their efficiencies in corrosive media. The presence of a heteroatom in an OGCI molecule enhances their adsorption onto the metal surface through the formation of an adsorptive bond by Lewis acid-base reaction in which OGCI and metal act as electron donor and acceptor, respectively. The strength of an adsorption bond is a function of electron density and polarizability of the reaction center. Conclusively, studies have shown surface-active OGCI adsorption to increase with increasing molecular weight and dipole moment.

Table 1: Some attaching functional groups in OGCI (Singh, 1993).

Functional group	Name	Fuctional group	Name
-OH	Hydroxy	-NH ₂	Amino
-C-N-C-	Amine	-SH	Thiol
-NO ₂	Nitro	-C≡C-	-yne
-CONH ₂	Amide	-S=O	Sulfoxide
-COOH	Carboxy	-NH	Imino
-S-	Sulfide	-N=N-N-	Triazole
-C=S-	Thio	-C-O-C-	Epoxy
-P=O	Phosphonium	-P-	Phospho
-Se-	Seleno	-As-	Arsano

Table 2: Sources of OGCI, functional groups, and corrosion inhibitory roles.

OGCI source	Functional groups and compounds	Corrosion inhibitory roles	References
<i>G. biloba</i> leaf extracts	Flavonoids and terpenoids; phenol groups and aromatic rings	Terpenoids: quercetin adsorption on mild steel surface based on the interactions of donor-acceptor between O and aromatic ring <i>p</i> -electrons and surface iron vacant <i>d</i> -orbitals Flavonoids: oxygen-adsorption corrosion inhibited via its oxidation to benzoquinone by O ₂ resolved in the solution	Chen et al., 2013
<i>Rothmannia longiflora</i> extract	Monomethyl fumarate, 4-oxonicotinamide-1-(1-β-D-ribofuranoside), and D-mannitol	–	Akalezi et al., 2015
<i>Petersianthus macrocarpus</i> plant	Petersaponin, β-sitosterol, and ellagic acid	Molecules are adsorbed on the surface of mild steel surface as a result of hydroxyl group and aromatic ring protonation. Constituent molecules have aromatic rings (π-electrons) with attached electron releasing groups. Also, the increase of the ability of π-electrons to be bonded to vacant <i>d</i> -orbital in Fe	Akalezi et al., 2015
Extract of <i>Ficus asperifolia</i>	Saponins, alkaloids, tannins, anthraquinones, flavonoids, reducing sugars, <i>n</i> -hexane, ethyl acetate, and butanol	The electron-donating ability was facilitated as a result of rich bond or heteroatoms present in the chemical structures. Thus, the formation of complexes on the material surface to inhibit corrosion was enhanced	Ebenso et al., 2008
Extracts of <i>D. kaki</i> L.f husk	Vitamins, <i>p</i> -coumaric acid, gallic acid, catechin, flavonoids, carotenoids, and condensed tannin	–	Zhang et al., 2013
Gum arabic	Arabinogalactan, oligosaccharides, polysaccharides, and glucoproteins	–	Umoren et al., 2006
Tobacco extract	Polyphenols, terpenes, alkaloids, alcohols, carboxylic acids, and nitrogen-containing compounds	Corrosion inhibition on metals by electrochemical activity due to fused benzene ring system with charge dislocation property	Rudresh and Mayanna, 1977
Extract of green wild jute tree (<i>Grewia venusta</i>)	Polysaccharides, polyphenols (catechins and flavonoids) vitamins, tannins, minerals, volatile oils, and alkaloids	Mixed inhibitor corrosion inhibition action	Suleiman et al., 2013
<i>Anthocleista djalonensis</i>	Iridoid glucoside (DJN), dibenzo-α-pyrone (djalonsone), ursolic acid, and 3-oxo-Δ ⁴ ,5-sitosterone	–	Obame et al., 2008
Guar gum	Polysaccharides, mainly sugars galactose and mannose	1,4-Linked mannose residue linear chain-forming short-side branches, which later formed complexes on the metal surface to inhibit corrosion	Abdallah, 2004
<i>Jatropha curcas</i> leaf extract	Tannins, flavonoids, terpenes, anthraquinone, apigenin, cardiac glycoside, alkaloids, deoxy sugar, saponins, α-D-glucoside, sterols, stigmasterol, and vitexin	Corrosion inhibition via the formation of continuous complex metal ions on the metal surface by polar groups	Ejikeme et al., 2014; Rani and Selvaraj, 2014
Extracts of banana peel	Bananadine (3Z,7Z,10Z)-1-oxa-6-azacyclododeca-3,7,10-triene	–	Sangeetha et al., 2012
<i>Aloe vera</i> plant extract	Minerals, polysaccharides, vitamins, glycoproteins, and enzymes	–	Gupta et al., 2018
<i>Azadirachta indica</i>	Azadirachtin, salannin, meliantriol, and nimbin	Inhibition effects due to electronic, geometry coupled with binding property bases on the metal surface	Sharma et al., 2015
Locust bean gum	Galactomannan-type polysaccharides	–	Jano et al., 2012
Oil palm frond	Phenolic constituents (<i>p</i> -hydroxybenzoic acid, syringic acid, vanillic acid, vanillin, <i>p</i> -hydroxybenzaldehyde, <i>p</i> -hydroxyacetophenone, and syringaldehyde)	Lignin is cleaved to form aromatic carbonyl compounds (syringaldehyde and vanillin) via alkaline nitrobenzene oxidation to inhibit corrosion	Yokoi et al., 2001

Table 2 (continued)

OGCI source	Functional groups and compounds	Corrosion inhibitory roles	References
<i>J. gendarussa</i> plant extract	Friedelin, β -sitosterol, <i>o</i> -substituted aromatic amines lupenol, phenolic dimmers, and flavonoids	Corrosion inhibition of metal as a result of mixed-type inhibitor actions	Satapathy et al., 2009
Leaf and flower extracts of <i>Heliconia rostrata</i>	Alkaloids, flavonoids, tannins, cellulose, and polycyclic compounds	The presence of heterocyclic constituents enhanced film formation over the metal surface, thus affording corrosion inhibition	—
Celery (<i>Apium graveolens</i>) seeds	Flavonoids, linoleic acid, D-limonene, sesquiterpene alcohols, coumarins, selenine, sedanolide, and sedanonic anhydride	—	Megahed et al., 2017
Henna extract (<i>Lawsonia inermis</i>)	Lawsonone, α -D-glucose, gallic acid, and tannic acid	Mixed-type corrosion inhibition mechanism with constituents order of inhibition efficiency of tannic acid < α -D-glucose < gallic acid < henna extract < lawsonone	Ostovari et al., 2009

1.5 Measuring OGCI efficiency

The first step required in measuring the efficiency of OGCI is the preparation of a metal sample to be examined for corrosion. The selection of metal coupons for checking OGCI efficiency is vital as small changes in metal composition or available impurities during fabrication are reflected in the obtained results (Qian et al., 2013). The metal composition should as much as possible be relevant to metals related to the corrosion problem. Of all the available methodologies for measuring OGCI efficiency in the literature, weight loss measurement (WLM), electrochemical impedance spectroscopy (EIS), linear polarization resistance, and potentiodynamic polarization (PDP) are the prominent ones.

1.5.1 WLM

Many researchers used test solutions prepared from actual field solution for corrosion testing, whereas some used synthetic solutions prepared from analytical-grade reagents in the absence of the former for WLM. Before OGCI efficiency is determined using WLM, metal samples are cleaned by polishing with abrasive paper of different grades and washed thoroughly using solvents (acetone, ethanol, and distilled water) after which they are dried at room temperature. Vernier caliper is used to measure the dimensions of the metal specimen. The prepared metal coupons are then weighed before immersion using high-accuracy digital balance. The thoroughly rinsed corroded metal coupons are reweighed after a specified period of exposure time to check the weight loss. The corrosion rate (Ostovari et al., 2009), surface coverage θ (Al-Zubaidi et al., 2016), and percent corrosion inhibition efficiency $\eta\%$ (Yaro et al., 2013) can then be evaluated using Eqs. (4)–(6), respectively. The influence of OGCI in preventing corrosion attack of the metal coupons is checked by sample WLM in the absence and presence of OGCI. The WLM technique is simple and reliable as it forms the basic fundamental method of measuring OGCI efficiency in many corrosion-monitoring programs.

$$CR = \frac{w_1 - w_2}{At} \quad (4)$$

$$\theta = \frac{w_1 - w_2}{w_1} \quad (5)$$

$$\eta\% = \frac{w_1 - w_2}{w_1} \times 100\% \quad (6)$$

where CR =corrosion rate ($\text{g}/\text{cm}^2/\text{h}$), w_1 =metal coupon weight loss in the absence of OGCI (g), w_2 =metal coupon weight loss in the presence of OGCI (g), A =metal coupon surface area (cm^2), and t =immersion time (h).

However, there are cases where the inhibition efficiency of OGCI is enhanced as a result of the combination with another OGCI such that the inhibition efficiency is increased by an appreciable value. This is called synergism effect, which can be quantified using Eq. (7) (Murakawa et al., 1967):

$$S = \frac{1 - \theta_A - \theta_B + \theta_A \theta_B}{1 - \theta_{AB}} \quad (7)$$

where θ_A and θ_B =respective surface area coverage by compounds A and B when acting separately and θ_{AB} =surface area coverage obtained for the mixture of A and B. When S approaches 1, the interaction between A and B is negligible. If $S > 1$, it reveals the existence of synergism, whereas $S < 1$ signifies an opposite effect between A and B (Mobin and Rizvi, 2016).

1.5.2 PDP

PDP is another means of measuring OGCI efficiency, corrosion rate, and corrosion mechanism protection through electrochemical-based measurements. In most cases, the basic laboratory setup involves using three electrodes in the electrochemical cell, which are working, counter, and reference electrodes for the measurement immersed in the test solution of known volume and concentration. Platinum electrode (Shah et al., 2017) and graphite rod (Al-Zubaidi et al., 2018) are mostly used as the counter electrode, whereas saturated calomel electrode (Akalezi et al., 2015) and Ag/AgCl aqueous electrode are used as the reference electrode. The working electrode is the metal substrate under examination. The voltage (V) of the system is measured and controlled by the reference electrode, whereas the current (I) is measured by the counter electrode. As the electrochemical reactions progress, open circuit potential (E_{ocp}) of the metal fluctuates. At equilibrium, a stable value is then measured after which a PDP scan is performed. After this, a Tafel plot is obtained by applying a potential from a value below the initially measured E_{ocp} to a higher potential (between -0.25 and $+0.25$ V). The corrosion current (i_{corr}) and corrosion potential (E_{corr}) are then measured from the plots. Figure 3 represents the typical polarization curves for Q235A steel corrosion in 1 M HCl in the absence and presence of varying concentrations of persimmon husk extracts as OGCI. Corrosion rate

Figure 3: Polarization curves for Q235A steel corrosion in 1 M HCl in the absence and presence of varying concentrations of persimmon husk extracts as OGCI (Zhang et al., 2013).

is measured using Eq. (8) (Al-Sabagh et al., 2012), whereas $\eta\%$ is calculated by measuring i_{corr} in the presence and absence of OGCI using Eq. (9) (Verma et al., 2015):

$$CR = \frac{i_{\text{corr}} \times \kappa \times EW}{\rho \times A} \quad (8)$$

$$\eta\% = \frac{i_{\text{corr}}^0 - i_{\text{corr}}^1}{i_{\text{corr}}^0} \times 100\% \quad (9)$$

where κ =conversion factor, EW =equivalent weight (g), ρ =density (g/cm^3), A =sample area (cm^2), and i_{corr}^0 and $i_{\text{corr}}^1 = i_{\text{corr}}$ density values in the absence and presence of OGCI molecules, respectively.

1.5.3 EIS

EIS is an essential method of monitoring *in situ* electrochemical changes with critical understanding of physical processes occurring at the metal-electrolyte interface (Mourya et al., 2014) such that information related to electrode kinetics, surface properties, and mechanistic can be taken from impedance diagrams (Lorenz and Manfield, 1981). Just like PDP, the experiment is conducted in a three-electrode electrochemical cell with small potential upsetting between 5 and 50 mV of AC voltage over frequency variation between 100 kHz and 10 mHz (Ramanavicius et al., 2010). The EIS parameters are obtained using experimental EIS spectral (Nyquist plot) obtained with the aid of suitable circuits from values of frequencies that correspond to real (Z') and

imaginary (Z'') impedance values. A typical Nyquist plot for examining mild steel in 1 M H_2SO_4 at 30°C by means of a new Schiff base extract with different concentrations as OGCI is shown in Figure 4. The adopted equivalent circuit comprises R_s (electrolyte solution resistance), in series with a parallel arrangement of constant phase element (CPE) and R_{ct} (charge transfer resistance; Roy et al., 2014) modeled in a system of metal substrate, adsorbed inhibitors, and electrolyte solution.

However, one study has used polarization resistance (R_p) obtained as real impedance difference at reduced and higher frequencies to replace the usual R_{ct} (Gupta et al., 2018). R_p is noticed to include R_{ct} , accumulation resistance (R_a) resulting from species accumulated at the metal-electrolyte interface, diffusion layer resistance (R_d), and inhibitor film resistance (R_i) on the metal surface. Anode-cathode charge transfer causes metal oxidation, which is usually obstructed by the presence of solvent molecules in aqueous acid solution. The resistance by the electrolyte solution is called the solution resistance (R_s). R_{ct} represents the protective film capacity of adsorbed organic molecules on the metal surface to impede charge transfer to the metal-solution interface. Impedance parameters that include R_p , n , C_{dl} , and $\eta\%$ can then be obtained from a Nyquist plot by the equivalent circuit.

Figure 4: Mild steel Nyquist plot in 1 M H_2SO_4 at 30°C for varying OGCI concentrations (Al-Amiery et al., 2014).

For a better explanation of a frequency-independent phase shift existing between an applied alternating potential and its current response, a CPE represented mathematically as Eq. (10) is used instead of capacitance (C ; Satapathy et al., 2009):

$$Z_{\text{CPE}} = \frac{1}{A} (j\omega)^{-n} \quad (10)$$

where Z_{CPE} = CPE impedance, A = CPE constant, ω = angular frequency, j = imaginary number (i.e. $i^2 = -1$), and n = phase shift exponent that is a measure of surface irregularity/inhomogeneity. The significance of n is that a lower surface roughness is obtained at a higher n and vice versa. Also, n determines the nature of CPE and states what A in Eq. (10) represents as briefly summarized in Table 3. Electrical double-layer capacitance values can be calculated using any of Eqs. (11)–(13), whereas percent inhibition efficiency $\eta_E(\%)$ in the presence and absence of OGCI is determined by Eq. (14) (Shah et al., 2017):

$$C_{dl} = (AR_{ct}^{1-n})^{\frac{1}{n}} \quad (11)$$

$$C_{dl} = A(\omega_{\text{max}})^{n-1} \quad (12)$$

$$C_{dl} = \frac{1}{2\pi\omega_{\text{max}}R_{ct}} \quad (13)$$

$$\eta_E(\%) = \frac{R_{ct(i)} - R_{ct(o)}}{R_{ct(i)}} \times 100\% \quad (14)$$

where ω_{max} = maximum frequency of impedance imaginary quantity (rad/s) and $R_{ct(i)}$ and $R_{ct(o)} = R_{ct}$ in the presence and absence of OGCI various concentrations, respectively.

In general, Table 4 summarizes the significance/implication of changes in trends and variations in the values of parameters associated with the techniques of measuring OGCI efficiencies as observed in previous studies.

Table 3: Significance of n values on the CPE nature.

n	CPE nature (A)	Significance	References
0	Resistance	A metal-solution interface operating as a resistor	Bai, 2015
1	Capacitance	Plane and homogeneous electrode surface with the metal-solution interface behaving as a capacitor with a regular surface	Lin et al., 2015
−1	Inductance	Nonplane and heterogeneous electrode surface with the metal-solution interface behaving as an inductor with an irregular surface	Deyab et al., 2007
1/2	Warburg impedance	A metal-solution interface acting as both capacitor and inductor	Yurt et al., 2006

Table 4: Summary of the significance of parameter variations obtained from methods of measuring OGCI efficiencies as observed in previous studies.

Observation	Significance/implication	References
WLM		
Inhibition efficiency increases as OGCI concentration increases	The adsorption of enough molecules of OGCI on the metal surface at higher concentration causes higher surface coverage	Akalezi et al., 2015
The inhibition efficiency of OGCI “A” in combination with a small concentration of OGCI “B” is higher than the summation of inhibition efficiencies of OGCI “A” alone	The synergism parameter is greater than 1, which suggests better corrosion protection metallic specimens by OGCI “A + B” than using OGCI “A” alone	Mobin and Rizvi, 2016
The inhibition performance of OGCI molecules decreased with increasing solution temperatures	1. This resulted from an increased mobility of OGCI molecules, which decreased the existing interaction between the metal surface and OGCI molecules 2. Rapid etching, molecular rearrangement, and/or fragmentation and desorption of adsorbed OGCI molecules at higher temperature might decrease inhibition efficiency	Bai, 2015
PDP		
Change of E_{corr} values to more negative values in different OGCI concentrations coupled with a decrease in cathodic and anodic current density with increasing OGCI concentrations	Adsorption of molecules of OGCI on the sample surface, forming a protective metal surface. Cathodic polarization occurred. Anodic polarization occurs when anode potential shifts to positive direction. $E_{\text{corr}} > 85$ mV implies anodic or cathodic OGCI, whereas E_{corr} displacement of < 85 mV means mixed-type OGCI	Ahamad et al., 2010; Khadom et al., 2010
Increase in OGCI concentrations causing reduction of i_{corr} density (i_{corr}) with increase in inhibition efficiency (IE)	OGCI is effective in protecting the metal in acidic medium solution	Kartsonakis et al., 2012
Cathodic Tafel slope (β_c) and anodic Tafel slope (β_a) changed due to the addition of OGCI	OGCI influences anodic and cathodic reactions	Bilgic and Caliskan, 2001
Anodic and cathodic branches of Tafel plot shifted to lower values for all examined concentrations of OGCI added	Organic constituents of OGCI inhibited both hydrogen evolution (cathodic reaction) and metal dissolution (anodic reaction), suggesting that OGCI acted as mixed type	Obot et al., 2009
EIS		
Significant increase in R_p value as a result of adding inhibitor	Charge transfer reaction retarded by inhibitors and corrosion occurring on the metal surface with the formation of a protective film	Solmaz et al., 2008
Reduction of C_{dl} values due to the presence of inhibitor molecules	1. This resulted from local dielectric constant decrease and/or electrical double-layer thickness increase 2. Also, surface metal inhibition resulted from adsorption mechanism by the replacement of water molecules 3. Increase in surface coverage by OGCI causing an increase in inhibition efficiency	Yousef et al., 2015
Imperfect semicircle obtained in Nyquist plots when the concentration of OGCI increases in the solution	This is attributed to metal surface imperfections and roughness called the dispersing effect	Tang et al., 2009
Phase angle values in Bode plot for inhibited metallic specimens higher than uninhibited specimen	Surface becomes appreciably smooth due to protective film formation by OGCI over the metal surface	Verma et al., 2015
Increase in Nyquist plot diameter with increasing OGCI concentration	This indicates inhibitive film strengthening with decrease in corrosion rate	De Souza and Spinelli, 2009
Nyquist plot containing a depressed semicircle for used solid electrode	This is linked to metal electrode inhomogeneities and surface roughness	Raja and Sethuraman, 2008
Significant increase in R_{ct} in the presence of OGCI molecules	Adsorption of OGCI molecules on the metal surface. High corrosion protection efficiency	Amin and Ibrahim, 2011
Decrease in Nyquist plot diameter with increasing solution temperature	Corrosion inhibition rate decreases with an increase in solution temperature	Al-Amieri et al., 2014
Decrease in values of R_{ct} and IE as a result of an increase in temperature	Adsorbed OGCI molecules on the metal surface subjected to desorption with continuity in an increase of solution temperature	Fouda et al., 2006

Table 4 (continued)

Observation	Significance/implication	References
Values of slope and phase angle deviating from the ideal capacitive behavior of the electric double layer (slope = 1 and phase angle = -90°) in the Bode impedance and phase angle plots for inhibited and uninhibited metallic specimens	This resulted from metal surface inhomogeneity	Singh et al., 2016

2 Previous studies on using OGCI

Table 5 summarizes the literature consulted for different OGCI sources used for testing various kinds of metallic materials in different corrosive media, extraction methodology, employed characterization of OGCI, findings, and prospective future challenges.

2.1 Industrial applications of OGCI

Industrial applications of corrosion inhibitors from greeners can be found in petroleum production, steel pipeline-making industry, refrigeration industry, automobile, paint industry, acid-producing companies, and so on. Table 6 summarizes the industrial applications of OGCI with active functional groups responsible for each application.

3 Mathematical modeling of OGCI influence on metals

3.1 Kinetics of corrosion modeling

3.1.1 Anodic modeling

To model the kinetics of corrosion at the anode, the following assumptions are made: (1) anodic i_{corr} density is used for Fe^{2+} ion boundary condition at anode, (2) anodic i_{corr} density accounts for Fe^{2+} ion generation via electrochemical reactions on the metal surface as the source term, (3) zero concentration of Fe^{2+} ion is applied at cathode due to scale formation, (4) Fe^{2+} ion concentration in the shielded solution is the same as bulk solution in chemical equilibrium, and (5) H^+ (C_{H^+}) and CO_2 (C_{CO_2}) surface concentrations enhance the rate of corrosion via exchange current density. Thus, the anodic electrochemical reaction is given as Eq. (15) (Popoola et al., 2013):

The anodic i_{corr} density is calculated using Eq. (16) (Tafel's law):

$$i_{\text{Fe}^{2+}} = i_{0,\text{Fe}^{2+}} \cdot 10^{\frac{\phi_a - \phi_{\text{rev,Fe}^{2+}}}{b_{\text{Fe}^{2+}}}} \quad (16)$$

where $i_{\text{Fe}^{2+}}$ = iron oxidation current density (A/m^2), $i_{0,\text{Fe}^{2+}}$ = iron oxidation exchange current density (A/m^2), ϕ_{rev} = reversible potential of iron oxidation (V), ϕ_a = anodic potential (V), and b = Tafel slope of oxidation (V).

The iron oxidation exchange current density ($i_{0,\text{Fe}^{2+}}$) in Eq. (16) is determined from Eq. (17) (Nordsveen et al., 2003):

$$i_{0,\text{Fe}^{2+}} = i_{0,\text{ref}} \left(\frac{C_{\text{H}^+}}{C_{\text{H}^+,\text{ref}}} \right)^{a_1} \cdot \left(\frac{C_{\text{CO}_2}}{C_{\text{CO}_2,\text{ref}}} \right)^{a_2} \cdot e^{\frac{-\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right)} \quad (17)$$

where $i_{0,\text{ref}}$ = reference exchange current density (A/m^2), C_{H^+} = surface concentration of hydrogen ion (mol/l), $C_{\text{H}^+,\text{ref}}$ = reference hydrogen ion concentration (mol/l), C_{CO_2} = surface concentration of CO_2 (mol/l), $C_{\text{CO}_2,\text{ref}}$ = reference CO_2 concentration (mol/l), ΔH = change in enthalpy (kJ/mol), R = gas constant (J/mol K), T = solution temperature ($^\circ\text{K}$), and T_{ref} = reference temperature ($^\circ\text{K}$).

The mass flux of Fe^{2+} at anode ($J_{\text{Fe}^{2+}}$) is determined by Eq. (18) (Gavrilov et al., 2007):

$$J_{\text{Fe}^{2+}} = \frac{i_{\text{Fe}^{2+}}}{n_{\text{Fe}^{2+}} F} \quad (18)$$

where $J_{\text{Fe}^{2+}}$ = mass flux of Fe^{2+} at anode ($\text{mol/m}^2 \text{ s}$), $i_{\text{Fe}^{2+}}$ = current density of iron oxidation (A/m^2), F = Faraday's constant (C/mol), and $n_{\text{Fe}^{2+}}$ = number of moles of Fe^{2+} (mol).

3.1.2 Cathodic modeling

The derivation of equations governing the kinetics of corrosion at the cathode is based on the assumption that oxygen and water reduction in the system is negligible

Table 5: Summary of literature on sources of previously used OGCI.

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
<i>Camellia sinensis</i> (green tea)	Dried and ground leaves subjected to reflux in 70% acetone for 4 h	Mild steel in 1 M HCl	SEM, EIS, WLM, FTIR, EDX	1. 79% inhibition efficiency achieved in 200 ppm solution 2. Inhibition effect increases with an increase in solution concentration and temperature	Adsorption kinetics and isotherms studies were not examined	Nofrizal, 2012
<i>R. longiflora</i> extract	Extraction	Mild steel in 1 M HCl and 0.5 M H ₂ SO ₄	PDP, EIS	Increase in corrosion inhibition efficiency as extract concentration and temperature increase	1. Extraction methodology was not presented 2. Extract was not characterized for functional groups inhibiting corrosion	Akalezi et al., 2015
<i>A. djalonesis</i> leaf extract	20 g dried leaves under reflux for 3 h in 1 M HCl and 0.5 M H ₂ SO ₄	Mild steel in 1 M HCl and 0.5 M H ₂ SO ₄	EIS, PDP, DFT-based QCC	1. Corrosion inhibition via mixed-type inhibition mechanism 2. Djaloneside (DJN) and its hydrolysis product DJN-hyd were extracts enhancing corrosion inhibition in the medium 1. Increase in corrosion inhibition efficiency as OGCI concentration increases but decreased with temperature	Corrosion of other metals besides mild steel was not investigated	Ogukwe et al., 2012
<i>Theobroma cacao</i> peel polar extract	Boiling dried pods under reflux for 4 h in 1.0 M HCl	Mild steel in 1 M HCl	WLM, EIS, PDP	1. Increase in corrosion inhibition efficiency as OGCI concentration increases but decreased with temperature 2. Langmuir isotherm was obeyed	More metallic materials should be tested	Yetri et al., 2014
<i>o,m,p</i> -Decanoyl thiourea derivatives	Mixed substitution and addition reaction using decanoyl chloride, ammonium thiocyanate, and 2-aminopyridine in acetone solution for 10 min	Mild steel in 0.1 M H ₂ SO ₄	FTIR, ¹ H and ¹³ C NMR	1. Compound D3 of the derivatives possessed the highest efficiency 2. Compound corrosion inhibition efficiencies affected by N atom at <i>o</i> -, <i>m</i> -, and <i>p</i> -positions affects the pyridine chemical structure	1. Only mild steel was considered 2. Limited laboratory analysis 3. Although chemical structures were presented, the structural morphology of the synthesized inhibitors need be investigated	Kamal et al., 2014
Extracts of <i>D. kaki</i> L.f husk	Husk powder heated under reflux with water or alcohol for 4 h	Q235A steel in 1 M HCl	PDP, GM	1. Extracts behaved like a mixed-type inhibitor 2. Extracts exhibited antibacterial activity against microbial influenced corrosion (MIC) of oil field microorganism	1. There is a need to fully explore the corrosion inhibitory feature of extracts from this biomass in other corrosion types besides microbial influenced corrosion 2. SEM analysis was not carried out to ascertain that the corrosion type inhibited on the metal surface by the extracts was exactly MIC	Zhang et al., 2013
Schiff bases	8 h refluxing of 3-amino-2-methylquinazolin-4(3 <i>H</i>)-one with 4-hydroxybenzaldehyde and <i>N,N</i> -dimethyl-4-aminobenzaldehyde in acetic acid	Mild steel in 1.0 M HCl	SEM, NMR, DFT	1. <i>p</i> -position substituent enhanced inhibition efficiency 2. Inhibition efficiency relies on OGCI nitrogen amount and their molecular weight and concentration	1. <i>m</i> -position substituent on OGCI molecule affected inhibition efficiency negatively 2. Corrosion type prevented was not specified 3. Only mild steel was used to test the inhibitor efficiency	Jamil et al., 2018

Table 5 (continued)

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
<i>G. biloba</i> leaf extracts	Powder was heated with water or alcohol for 4 h after drying under 60°C	Q235A steel in 1 M HCl	PDP	<ol style="list-style-type: none"> 1. Extracts exhibited mixed-type inhibitor behavior 2. Extract revealed antibacterial activity against oil field microorganism 	<ol style="list-style-type: none"> 1. More laboratory analysis is required to corroborate the findings 2. Although corrosion mechanism and antibacterial activity of the extracts were presented, the adsorption and kinetic studies of the process are needed in future studies 	Chen et al., 2013
<i>Musa sapientum</i>	–	Mild steel in 0.5 M H_2SO_4	ECM	<ol style="list-style-type: none"> 1. Decrease in corrosion rate as inhibitor concentration increases 2. Physisorption was experienced 	<ol style="list-style-type: none"> 1. Only acidic medium was examined 2. Reaction kinetics was not studied 3. Limited laboratory analysis 	Salami et al., 2012
Isoxazolidine derivatives of aldehyde	Nitrone cycloaddition reaction	Mild steel in 1 M HCl, 0.5 M H_2SO_4 , CO_2 -saturated 0.5 M NaCl	GM, LPR, TEM, EIS, ST	<ol style="list-style-type: none"> 1. Inhibitor molecules primarily acted as anodic inhibitors 2. Adsorption of inhibitors on the metal surface was due to physisorption and chemisorption 3. Surface tension revealed the formation of film on the metal surface by inhibitor molecules 4. Inhibitor molecules fitted well using Temkin isotherm in both acids 5. Langmuir isotherm performed excellently in CO_2-saturated saline media 	<ol style="list-style-type: none"> 1. Solution media were not tested in the absence of synthesized inhibitors for comparison purposes 2. The kinetics of the process was not studied 	Mazumder and Jafar, 2016
Hydroxyethyl-imidazoline derivatives based on coffee oil	–	Carbon steel in CO_2 -saturated emulsion at 50°C	CO_2 -EIS	<ol style="list-style-type: none"> 1. Inhibitor decreased corrosion rate by >99.9% 2. Unprotected sites were linked to electrostatic repulsion forces between the negative charges and insufficient added concentration to form protective film 	<ol style="list-style-type: none"> 1. Unprotected sites were formed on the metal surface 2. Reference was made to a previous study for synthetic methodology used 3. Only EIS was used to check inhibitor efficiency 	Porcayo-Calderon et al., 2015
<i>Sida acuta</i> (Malvaceae) leaves	Immersion of pounded leaves into HCl at 15, 30, and 45 g/l of 0.7, 1.2, and 2.2 M HCl	Mild steel in 0.7, 1.2, and 2.2 M HCl	WLM	<ol style="list-style-type: none"> 1. 71.16% maximum inhibition efficiency attained at 15 g/l of 0.7 M HCl with corrosion rate reduction from 1.0485 to 0.3006 mg/cm²/h 2. Phytochemical analysis revealed the presence of alkanoids, tannins, saponins, phytates, flavonoids, and phenol 3. Out of the examined isotherms, experimental data fitted well into Langmuir 	<ol style="list-style-type: none"> 1. SEM image revealed the degradation of mild steel surface in an uninhibited 0.7 M HCl to be localized 2. Only WLM as a means of checking inhibitor efficiency was used 3. Only acidic medium 4. Only mild steel 	Ndukwe and Anyakwo, 2017

Table 5 (continued)

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
<i>P. macrocarpus</i> plant	Boiling dried leaves under reflux for 3 h in 1.0 M HCl and 0.5 M H_2SO_4	Mild steel in 1 M HCl and 0.5 M H_2SO_4	GM, PDP, EIS	<ol style="list-style-type: none"> 1. EIS data revealed organic matter extract influence on corrosion inhibitory effect on mild steel 2. Inhibition efficiency increased with an increase in concentration and temperature up to 50°C 3. Lower activation energy in the presence of corrosion inhibitor resulted from the adsorption chemisorptive nature 	<ol style="list-style-type: none"> 1. The influence of the inhibitor in alkaline medium was not investigated 2. Only mild steel was examined 3. The kinetics of the process was not studied 4. The efficiency of the inhibitor used was not compared to those of previous inhibitors used by the researchers 	Akalezi et al., 2015
<i>Hibiscus rosa-sinensis</i> leaf extract	–	Mild steel in 1 M HCl	WLM, EIS	<ol style="list-style-type: none"> 1. Inhibition efficiency increased as temperature and solution concentration increased 2. OGCI behaved as mixed type 3. Spontaneous reaction 4. Data agreed well with Langmuir, Flory-Huggins, and Freundlich adsorption isotherms 	<ol style="list-style-type: none"> 1. Limited laboratory analysis to affirm the inhibitor efficiency 2. Only mild steel in only acidic medium was investigated 	Desai, 2015
D-glucose derivatives	Multicomponent reactions	Mild steel in 1 M HCl	SEM, EDX, AFM, EIS	The presence of -OH and -OCH ₃ groups exhibited higher inhibition efficiency	E_{ads} values did not exhibit any regular trend for aqueous and protonated inhibitor molecules	Verma et al., 2017
Silica extract from rice husk ash + Na ₂ O	Silica extract was prepared by mixing 80 ml of 2.5 M NaOH with rice husk ash produced by calcination at 600°C for 6 h. 0.2 M NaOH and distilled water were then added to form the inhibitor	99.9% Cu, Al alloy (AA6061), carbon steel (SAE1045) in 0.5 M HCl	XRF, XRD	<ol style="list-style-type: none"> 1. Each metal alloy influenced the optimal SiO₂:Na₂O ratio determination sodium silicate formulation 2. Used silicate-based inhibitor has a potential of inhibiting corrosion in tested samples under examined acidic medium 	<ol style="list-style-type: none"> 1. Limited laboratory analysis for more confirmation of inhibitor efficiency 2. Only acidic medium solution was tested 3. More metallic samples should be examined 	Mohamad et al., 2013
Gum arabic	–	Mild steel and Al in H_2SO_4	WLM, TT	<ol style="list-style-type: none"> 1. Inhibition efficiency increases with an increase in the concentration of the inhibitor 2. Inhibitor obeyed Temkin adsorption isotherm for tested samples 3. Mild steel corrosion was chemical adsorption, whereas Al corrosion was physical adsorption 4. Inhibitor acted better on Al than mild steel with adsorption being spontaneous 	<ol style="list-style-type: none"> 1. The methodology of inhibitor extraction was not adequately presented 2. The kinetics of the adsorption process was not presented 3. The reaction mechanism of the inhibitor adsorption process on mild steel and Al process was not available 4. Limited laboratory analysis to support inhibitor efficiency on samples 	Umoren, 2008

Table 5 (continued)

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
Coconut coir dust extract	Hydrogen evolution extraction method	Al corrosion in 1 M HCl	WLM, HEM	<ol style="list-style-type: none"> 1. As temperature and concentration increased, inhibition efficiency increased 2. Langmuir isotherm was obeyed 	<ol style="list-style-type: none"> 1. Only Al was considered. It would be better if inhibitor efficiency is tested in other metals 2. Also, only HCl as acidic medium was tested. Both acidic and alkaline solutions should be checked 	Umoren et al., 2006
<i>Jatropha</i> stem	<i>Jatropha</i> fine powder obtained by sun drying and grinding soaked in ethanol for 24 h. Evaporation of filtrate to remove excess alcohol	Mild steel in seawater	SEM, WLM, FTIR	<ol style="list-style-type: none"> 1. Coupons without inhibitor corroded more in seawater than those with inhibitor 2. Presence of active corrosion inhibitors <i>Jatropha</i> extracts revealed by FTIR 3. Maximum inhibition efficiency of 81.7% at 0.90 g/l inhibition concentration 	<ol style="list-style-type: none"> 1. Adsorption isotherm and thermodynamics were not studied 2. Few laboratory analysis for more affirmation of inhibitor efficiency 3. Inhibitor influence and efficiency in acidic and alkaline media were not investigated 	Olawale et al., 2016
Tobacco extract	Extraction by weighing aqueous solutions, boiling of water, and weighing residue	1008/1010 cold-rolled steel and 3105 H24 Al Q-panels in 1–3% NaCl solution	ZRA, PDP, WLM	<ol style="list-style-type: none"> 1. Tobacco extracts proved to be excellent inhibitors for the corrosion of Al and steel in alkaline solution 2. Extract also worked in acidic solution and could prevent corrosion during descaling processes 3. Inhibition effect greater than chromates with in a solution concentration range as low as 100 ppm 	<ol style="list-style-type: none"> 1. Thermodynamics, kinetics, and adsorption isotherm equilibrium of inhibitor effect were not investigated 2. Inhibition effect in other media was not investigated 	Davis et al., 2001
<i>Citrus aurantiifolia</i> leaves	Dried and ground leaves under reflux for 3 h in 1 M H ₂ SO ₄	Mild steel in 1 M HCl	SEM, WLM	<ol style="list-style-type: none"> 1. Corrosion inhibition increases with an increase in solution concentration with 97% efficiency 2. Experimental data conformed to Langmuir isotherm 	Only mild steel in acidic medium was investigated	Saratha et al., 2009
Cashew waste	Sun dried and pulverized fruits soaked in 250 ml ethanol for 24 h	Mild steel in 1 M HCl and 0.1 M H ₂ SO ₄	WLM, SEM, FTIR	<ol style="list-style-type: none"> 1. Inhibitor efficiency increased with an increase in inhibitor concentration with optimum 80.5% 2. Cashew waste was seen as a valuable corrosion inhibitor 	<ol style="list-style-type: none"> 1. Adsorption kinetics, isotherms, and thermodynamics were not studied for in-depth investigation 2. Only mild steel in acidic medium was investigated 	Olawale et al., 2015
Locust bean gum	–	Carbon steel 39, 44, and B500 in H ₂ SO ₄	PDP, EIS	Inhibition effect on steel 39 in acidic medium in the presence of NaCl was revealed	Although different carbon steel samples were tested, there was a shallow investigation on the extracted corrosion inhibitor on the examined samples	Jano et al., 2012
Extract of banana peel + Zn	–	Carbon steel in distilled water	AFM, WLM, GM, FTIR	Zn addition decreased inhibition efficiency. It later increases after increasing Zn concentration	No mathematical model was presented as a predictive tool for the future corrosion of the sample tested	Sangeetha et al., 2012

Table 5 (continued)

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
Fig leaf extract	Extraction by reflux in Soxhlet extractor for 5 h in alcohol	Mild steel in 2 M HCl	WLM, EIS	<ol style="list-style-type: none"> 1. Mixed-type inhibitor formed 2. Data support Langmuir isotherm 3. 87% inhibition efficiency with 200 ppm inhibitor solution 	Only mild steel in acidic medium was examined	Taleb and Mohamed, 2011
Rice straw extract	Reflux of 10 g rice straw in 100 ml of 1 M HCl for 1 h	Mild steel in 1 M HCl	EIS, PDP	<ol style="list-style-type: none"> 1. Physisorption of rice straw extract on mild steel electrode surface 2. Both anodic and cathodic reactions were inhibited, whereas OGCI exhibited mixed type 3. Adsorption data obeyed Langmuir isotherm 	<ol style="list-style-type: none"> 1. Few characterization of inhibitor extract 2. Only mild steel in HCl alone 	Mahross et al., 2016
<i>Dialium guineense</i> and <i>Euphorbia hirta</i> leaf extracts	Some grams of dried leaves subjected to reflux for some hours 0.5 M H ₂ SO ₄	Al alloy (AA8011) in HCl	GM	<ol style="list-style-type: none"> 1. Both extracts behaved as good inhibitors 2. Inhibition efficiency improved with concentration 3. Experimental data conformed with Langmuir adsorption isotherm 	Limited laboratory analysis for more investigation of inhibitor efficiencies	Anozie et al., 2011
Extract of <i>F. asperifolia</i>	Pulverized stem was obtained after oven drying at 40°C. Powdered stem bark was then soaked in 80% ethanol for 72 h	Mild steel in 5 M HCl	WLM, SEM, FTIR, AAS	<ol style="list-style-type: none"> 1. Inhibition efficiency increased with an increase in extract concentration but decreased with temperature 2. Inhibition of corrosion resulting from mixed plant constituent adsorption on the metal surface by spontaneous reaction 3. Extracts contain tannins, alkaloids, anthraquinones, flavonoids, saponins, and reducing sugars 4. Kinetic studies revealed that data agreed with first-order reaction 	<ol style="list-style-type: none"> 1. Although detailed kinetics, isotherm, and thermodynamic studies of adsorption process were presented, limited laboratory analysis for inhibitor characterization was done 2. Only mild steel in acidic medium was examined 	Fadare et al., 2016
Seeds of <i>Areca catechu</i>	After drying and grinding, seeds were subjected to reflux for 8 h in ethanol solution	Mild steel in 0.5 M HCl	WLM, PDP, EIS, SEM, FTIR	<ol style="list-style-type: none"> 1. Mixed-type inhibitor revealed 2. 96.97% corrosion inhibition achieved at 500 ppm inhibitor concentration 3. Experimental data agreed with Temkin isotherm 	<ol style="list-style-type: none"> 1. Only mild steel was examined 2. Higher inhibitor concentration required to achieved better corrosion inhibition 	Kumar et al., 2011
Elephant grass extract (<i>Pennisetum purpureum</i>)	10 g dried and pulverized leaves soaked in 100 ml ethanol for 48 h. Filtrates further subjected to evaporation to obtain ethanol-free sample	Mild steel in 1 M HCl	AAS, SEM, FTIR	<ol style="list-style-type: none"> 1. Steel dissolution rate sensitive to extract concentration in acidic solution. Mass loss and corrosion rates decreased with an increase in extract concentration 2. Inhibition influenced by absorption via the presence of extract functional groups 	Although detailed work was done, the inhibition effectiveness of elephant grass extract was only tested using mild steel in HCl as acidic medium	Alaneme et al., 2016

Table 5 (continued)

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
				3. Langmuir adsorption isotherms and activation energies revealed physical adsorption 4. SEM images of corroded substrates showed primary corrosion mechanism to be by pitting 5. 95% Inhibition efficiencies at room temperature achievable 6. Corrosion inhibition increased with an increase in extract concentration but decreased with increasing temperature 1. Increase in resistance of pitting corrosion was exhibited 2. Guar gum acted as a mixed-type inhibitor whose efficiency increases with an increase in concentration 3. All data supported Langmuir adsorption isotherm		
Guar gum	1. Pods dried in sunlight and separated manually from seeds 2. Seeds heated under reflux with water or alcohol for 6 h	Carbon steel in 1 M H_2SO_4 + NaCl	WLM, EIS, PDP		–	Abdallah, 2004
Oil palm frond	Nitrobenzene oxidation method for lignin depolymerization	Mild steel in 1 M HCl	WLM, PDP, EIS, SEM, XRD	1. Inhibition efficiency increased with increased concentration of lignin depolymerized products 2. Mixed-type inhibitors revealed 3. Experimental data well fitted with Langmuir adsorption isotherm 4. Adsorption was dominated by physisorption 5. SEM revealed reduction of surface roughness in the presence of an inhibitor 1. Optimum inhibition efficiency obtained at 500 ppm inhibitor concentration 2. Spontaneous adsorption process that conforms to Temkin isotherm 3. Percent inhibition efficiency decreased with increased temperature 4. Inhibition efficiency increased as celery doses increased	1. Only Langmuir isotherm was used. For comparative purposes, other existing isotherms should be used 2. Oil palm frond extracts have been shown to have potential of corrosion inhibition in alkaline medium. Thus, various types of metallic materials should be checked in alkaline medium	Shah et al., 2017
Celery seeds (A. <i>graveolens</i>)	Ground and powdered seed boiled in distilled H_2O for 2 h. Filtrate evaporated to dryness and residue used high concentrated stock solution	Carbon steel in 1 M HCl	WLM, PDP		1. Only WLM and PDP were used to check inhibitor efficiency 2. Only HCl was used for carbon steel alone to check OGCI efficiency 3. Active functional groups present in A. <i>graveolens</i> seeds enhancing corrosion inhibition were not deeply investigated	Megahed et al., 2017

Table 5 (continued)

OGCI source	Extraction methodology	Material tested; solution used	OGCI characterization; laboratory analysis	Findings	Future challenges	References
<i>Eichhornia crassipes</i> (water hyacinth) leaves and roots	4 g dried and ground leaves and roots soaked in 1000 ml of 5 M HCl	Mild steel in HCl	DFT, GT	1. Root and leaf extracts performed excellently well as effective OGCI 2. Physiosorption of extract organic constituents on corroding mild steel surface	1. Insufficient laboratory analysis 2. Equilibrium isotherms and kinetics were not investigated	Ulaeto et al., 2012
<i>G. venusta</i> plant extract	<i>G. venusta</i> cut into pieces, dried for 3 days, and ground into powder. Product was refluxed for some hours using ethanol	Mild steel in 0.5 M H_2SO_4	SEM	1. Corrosion rate was reduced when OGCI concentration was increased above 2% (v/v) with time 2. Increase in temperature massively increased corrosion rate 3. Plant extract exhibited effective corrosion inhibition potential for mild steel in acidic medium 4. At 8% (v/v) optimum concentration of plant extract in acid solution, 86.47% highest efficiency was obtained	1. Only SEM was used to authenticate inhibitor efficiency 2. Thermodynamics of adsorption process was not studied	Suleiman et al., 2013
Crude glycerol from residue of biodiesel produced from a plant seed	Transesterification process	Steel in 0.5 M HCl at 25°C	WLM, SEM, PDP	1. Corrosion inhibition increased with inhibitor concentration 2. Maximum inhibition efficiency of 98% was achieved after 70 h of residence time with 1% inhibitor concentration	1. Plant source of oil used for biodiesel production from which glycerol was obtained was not mentioned 2. Inhibition efficiency remained unchanged after residence time	Al-Zubaidi et al., 2018

AAS, Atomic absorption spectroscopy; AFM, atomic force microscopy; DFT, density functional theory; ECM, electrochemical measurements; EDX, energy-dispersive X-ray spectroscopy; FTIR, Fourier transform infrared; GM, gravimetric method; GT, gasometric technique; HEM, hydrogen evolution method; LPR, linear polarization resistance; NMR, nuclear magnetic resonance; QCC, quantum chemical computation; SEM, scanning electron microscopy; ST, surface tension; TEM, transmission electron microscopy; TT, thermometric techniques; XRD, X-ray diffraction; XRF, X-ray fluorescence; ZRA, zero-resistance ammeter.

Table 6: Industrial applications of OGCI's.

Industrial application	Active functional groups; complexes; ingredients	Inhibitor source from greener	%IE	How it works; how to solve the problem	Side effects	References
Petroleum production	Pyrocatechol 4-Methylpyrocatechol 4- <i>n</i> -Butylpyrocatechol 4- <i>n</i> -Hexylpyrocatechol		–14 84 93 96	Petroleum industries are characterized by wet corrosion of materials as a result of aqueous phase existence, which may contain H ₂ S, CO ₂ , and Cl [–] . The injection of these film-forming long-chain nitrogenous inhibitors anchors to the metal surface via existing polar group. The nonpolar tail extends out vertically such that the physisorption of hydrocarbons on them increases the thickness of the film coupled with hydrophobic barrier effectiveness to prevent corrosion	Emulsification occurs, which leads to foaming as a result of inhibitors being interfacial in nature	Uhlig and Revie, 1985
Steel pipeline internal corrosion	Galactose and mannose Iridoid glucoside and dibenzoyl- α -pyrone Flavonoids and terpenoids	Guar gum Leaf extract of <i>A. djalensis</i> <i>G. biloba</i> leaf extracts	86 97 98	Flow-induced corrosion and erosion-corrosion are influenced by the high flow rates of multiphase fluids in steel pipelines. At low flow rates, corrosion pitting occurs due to sediment formation at the bottom. The inhibitors being mixed type prevent corrosion by physical adsorption, chemisorption, and film formation. Also, the pigging of steel pipelines is employed to avoid internal corrosion	Due to mixed reaction, unwanted products and intermediates may be formed in the course, causing the formation of unwanted sediments	Abdallah, 2004; Obame et al., 2008
Automobiles	Phosphates and silicates Fatty acids, phosphonates, and sulfonates	Rice husk extract <i>D. kaki</i> L.f husk extracts Oil palm fond	92 95	The inhibitors dissolve in antifreeze to prevent internal corrosion caused by coolants, aeration, temperature, flow, and so on. External corrosion is controlled by mixing additives such as grease, wax resin, metalloorganic, and asphaltic compounds that enhance film formation on the metal surface	Foaming due to emulsification occurs	Zhang et al., 2013
Paint industry	Calcium plumbate, lead azelate, and lead suboxide	–		The displacement of water by polar compounds in inhibitors occurs after which they arrange themselves with hydrophobic ends facing the environment. The augmentation of coating bonding on the metal surface occurs after	Intermediate pigments may be formed	–
Water transmission industry	Phosphates, amine, volatiles (cyclohexylamine and morphine)	Tobacco extract	78.3	Inhibitors anchor to the metal using their polar group, which increases film thickness and hydrophobic barrier effectiveness for corrosion inhibition	The interaction between the organic inhibitor and water makes the water unsuitable for domestic usage in most cases	Abdel-Gaber et al., 2011

Table 6 (continued)

Industrial application	Active functional groups; complexes; ingredients	Inhibitor source from greener	%IE	How it works; how to solve the problem	Side effects	References
Refrigerating industry	Benzotriazole <i>p</i> -Hydroxybenzoic acid and vanillic acid	<i>A. dialanesis</i> Oil palm frond	88 67.8	Galvanic corrosion evolves due to the increase in dissolved mineral salt content as evaporation proceeds with the presence of several dissimilar metals and nonmetals. Inhibitors control corrosion by film formation that inhibits anodic metal dissolution reaction and cathodic poisoning When mixed with cement, the durability of reinforced concrete structures is improved Corrosion attack of pipes prevented by solubilization of limescale	-	Matsuda and Uhlig, 1964; Obame et al., 2008
Building construction Boiler	Phosphate ion Ammonia, alkanol, cyclohexylamine, and morpholine	- -	- -		- -	Yohai et al., 2013 Sanyal, 1981

such that the two cathodic reactions are stated as Eqs. (19) and (20) (Nesic et al., 1996):

A general form used in the calculation of H^+ reduction partial cathodic i_{corr} densities and H_2CO_3 reduction is stated as Eq. (21) (Nordsveen et al., 2003):

$$i_c = i_0 \cdot 10^{\frac{\phi_c - \phi_{\text{rev}}}{b}} \cdot \eta_{\text{Scale}} \quad (21)$$

where i_c = current density of any cathodic reaction (A/m^2), i_0 = cathodic reaction exchange current density (A/m^2), ϕ_c = cathodic potential (V), ϕ_{rev} = cathodic reaction reversible potential (V), b = cathodic Tafel slope (V), and η_{scale} = scale factor at cathode.

The exchange current densities of H^+ and H_2CO_3 reduction at cathode are determined using Eq. (17). The electric field in the solution is governed by Poisson's equation stated as

$$\nabla^2 \phi = -\frac{F}{\varepsilon} \sum_{i=1}^n z_i c_i \quad (22)$$

where ε = dielectric constant and ϕ = potential (V).

For electroneutrality condition in the solution, Eq. (22) reduces to

$$\sum_{i=1}^n z_i c_i = 0 \quad (23)$$

Thus, Eq. (23) reduces to

$$\nabla^2 \phi = 0 \quad (24)$$

3.1.3 Electrochemical modeling

Assuming that corrosion rate is governed only by electrochemical reaction, the total anodic reaction current density is used in determining the corrosion rate of CO_2 stated as (Nešić et al., 2009)

$$\text{CR} = \frac{i_a M_{\text{w,Fe}}}{\rho_{\text{Fe}} nF} \quad (25)$$

where CR = corrosion rate (mm/y), i_a = anodic current density (A/m^2), $M_{\text{w,Fe}}$ = atomic mass of iron (kg/mol), ρ_{Fe} = density of iron (kg/m^3), n = number of moles of

electrons involved in iron oxidation (2 mol/mol), and F = Faraday's constant.

The current density for iron dissolution is obtained by Eq. (26) stated as (Anderko and Young, 1999)

$$i_{a,Fe} = i_{o,Fe} \times 10^{\left[\frac{\alpha_{Fe} F (E_{corr} - E_{rev,Fe})}{RT} \right]} \quad (26)$$

The Tafel slope of iron oxidation b_{Fe} as defined as

$$b_{Fe} = \frac{RT}{\alpha_{Fe} F} \quad (27)$$

where R = ideal gas constant (J/mol K), T = temperature (K), F = Faraday's constant, and α_{Fe} = iron dissolution constant.

Thus, Eq. (26) reduces to

$$i_{a,Fe} = i_{o,Fe} \times 10^{\left[\frac{(E_{corr} - E_{rev,Fe})}{b_{Fe}} \right]} \quad (28)$$

where $i_{a,Fe}$ = current density for iron dissolution (A/m²), $i_{o,Fe}$ = exchange current density of iron oxidation (A/m²), E_{corr} = corrosion potential (V), $E_{rev,Fe}$ = reversible potential of iron oxidation (V), and b_{Fe} = Tafel slope of iron oxidation (V).

The current density of any cathodic reaction is calculated as (Craig, 1995)

$$\frac{1}{i_c} = \frac{1}{i_{ct}} + \frac{1}{i_{lim}} \quad (29)$$

where i_c = cathodic reaction current density (A/m²), i_{ct} = charge transfer current density component (A/m²), and i_{lim} = limiting current density component (A/m²).

The charge transfer current density of cathodic reactions (i_{ct}) is determined by (Chokshi et al., 2005)

$$i_{ct} = i_o \cdot 10^{\frac{\eta}{b_c}} \quad (30)$$

where i_o = exchange current density of cathodic reactions (A/m²), $\eta = E - E_{rev}$ is the overpotential (V), E = potential (V), E_{rev} = reversible potential (V), and b_c = cathodic Tafel slope (V/decade).

The limiting current is determined from the mass transfer limitation for the case of H^+ reduction. Thus,

$$i_{lim(H^+)}^d = k_m F \cdot [H^+]_b \quad (31)$$

where $i_{lim(H^+)}^d$ = diffusion limiting current density (A/m²), k_m = mass transfer coefficient of corrosive species (m/s),

$[H^+]_b$ = bulk hydrogen ion concentration (mol/m³), and F = Faraday's constant (96,490 C/equiv).

Suppose that there is a restriction of carbonic acid reduction due to CO_2 hydration reaction rate being very slow, the limiting current density ($i_{lim(H_2CO_3)}^r$) is calculated as (Vetter, 1961)

$$i_{lim(H_2CO_3)}^r = F \cdot [CO_2]_b \cdot (D_{H_2CO_3} K_{hyd} k_{hyd}^f)^{0.5} \quad (32)$$

where $[CO_2]_b$ = bulk concentration of dissolved CO_2 (mol/m³), $D_{H_2CO_3}$ = diffusion coefficient of H_2CO_3 in water (m²/s), K_{hyd} = equilibrium constant for CO_2 hydration reaction, and k_{hyd}^f = forward reaction rate constant for CO_2 hydration reaction (/s).

A theoretical flow multiplier f for Eq. (32), which takes into account the flow effect on the chemical reaction limiting current, is calculated by (Nešić et al., 2009)

$$f = \frac{1 + e^{-2\delta_m/\delta_r}}{1 - e^{-2\delta_m/\delta_r}} \quad (33)$$

where δ_m = mass transfer thickness (m) and δ_r = reaction layer thickness (r) whose values are determined by Eqs. (34) and (35), respectively:

$$\delta_m = \frac{D_{H_2CO_3}}{k_{m,H_2CO_3}} \quad (34)$$

and

$$\delta_r = \sqrt{\frac{D_{H_2CO_3} K_{hyd}}{k_{hyd}^f}} \quad (35)$$

3.2 Rate modeling of corrosion-type inhibition using OGCI

3.2.1 Pitting corrosion

The risk of pitting corrosion can be increased under stagnant conditions in which corrosive microenvironments are established on the surface. The accumulation of stagnant electrolyte at the bottom of pipes, tubes, and tanks can be prevented by both drying and ventilation. The build-up of local highly corrosive conditions can also be prevented through agitation (Roberge, 2000). The pitting corrosion rate, defined as Fe^{2+} ion mass flux leaving the metal surface, can be determined using Eq. (36) based on the following assumptions: (1) pitting corrosion results in the removal of Fe^{2+} ion from the metal surface by diffusion and electromigration and (2) Fe^{2+} ion distribution in the

solution is governed by Fick's second law. Thus, Fe^{2+} flux can be solved using Nernst-Planck equation (Papavinasam et al., 2005):

$$J_{\text{Fe}^{2+}} = -D_{\text{Fe}^{2+}} \nabla C_{\text{Fe}^{2+}} - \frac{Fz_{\text{Fe}^{2+}}}{\Re T} D_{\text{Fe}^{2+}} C_{\text{Fe}^{2+}} \nabla \phi \quad (36)$$

where J = mass flux ($\text{mol/m}^2 \text{ s}$), D = diffusivity (m^2/s), C = concentration (mol/l), F = Faraday's constant (C/mol), z = valence (mol/mol), $\Re$ = ideal gas constant (J/mol K), T = absolute temperature (K), and ϕ = electric potential (V).

The pitting corrosion rate is determined after computing the distributions of Fe^{2+} ion and electrical field in the solution such that change in concentration with time $\left(\frac{\partial C}{\partial t}\right)$ is determined as (Hoeppner et al., 1981)

$$\frac{\partial C}{\partial t} = -\nabla(J) + R \quad (37)$$

where R = source term of chemical reactions in the solution.

3.2.2 Stress corrosion cracking (SCC)

SCC in metallic materials has been discussed previously (Popoola et al., 2013). The outstanding models for predicting SCC rate are the active path dissolution and film rupture model and hydrogen-assisted cracking model. Active path dissolution occurs as a result of accelerated corrosion within a narrow path with higher corrosion susceptibility in comparison to the overall material or structure. In contrast, hydrogen-assisted cracking involves the entrapment of H atoms onto the metal crystal structure and the subsequent local cracking resulting from the local pressure build-up (Mohanty et al., 2012).

3.2.2.1 Active path dissolution and film rupture model

For this, the crack growth rate or crack velocity ($\dot{a}$) is given as (Ford and Andresen, 1988)

$$\dot{a} = \frac{da}{dt} = A(\dot{\epsilon}_{\text{ct}})^n \quad (38)$$

where A and n = constants related to the material and environmental composition at the crack tip and $\dot{\epsilon}_{\text{ct}}$ = crack tip strain.

The pure oxidation dissolution Faradic equation is stated as (Hall, 2009)

$$\dot{a} = \frac{da}{dt} = \frac{M}{z\rho F} i_t^a \quad (39)$$

where M = atomic weight, z = oxidation number, ρ = density (kg/m^3), F = Faraday's constant, and i_t^a = anodic current density at time t .

The anodic current density at time t is given as (Eason and Nelson, 1994)

$$i_t^a = i_o^a \left(\frac{t_o}{t} \right)^n \quad (40)$$

where i_o^a = base metal dissolution rate parameter and t_o = repassivation time scaling parameter (s or min or h).

Substituting Eq. (40) into (39) gives

$$\dot{a} = \frac{da}{dt} = \frac{M}{z\rho F} i_o^a \left(\frac{t_o}{t} \right)^n \quad (41)$$

If $a^* = \frac{M}{z\rho F} i_o^a$, Eq. (41) reduces to

$$\dot{a} = \frac{da}{dt} = a^* \left(\frac{t_o}{t} \right)^n \quad (42)$$

Integrating Eq. (42) over time from $t_o \rightarrow t_f$ and averaging the SCC growth rate over $t_f - t_o$, the average SCC growth rate is expressed as

$$\bar{a} = \frac{1}{t_f - t_o} \int \dot{a} dt = \frac{a^*}{1-n} \left(\frac{t_o}{t_f} \right)^n \quad (43)$$

where t_f = time per oxide fracture event (s or min or h) defined as

$$t_f = \frac{\epsilon_f}{\dot{\epsilon}_{\text{ct}}} \quad (44)$$

where ϵ_f = oxide film rupture strain rate and $\dot{\epsilon}_{\text{ct}}$ = crack tip strain rate.

Assuming that $\dot{\epsilon}_{\text{ct}}$ and t_f are constant and independent of time, Eq. (44) can be substituted in Eq. (43) to give the average SCC growth rate as

$$\bar{a} = \frac{a^*}{1-n} \left(\frac{t_o}{\epsilon_f} \right)^n (\dot{\epsilon}_{\text{ct}})^n \quad (45)$$

3.2.2.2 Hydrogen embrittlement

The related SCC model is based on the assumption that crack advance occurred due to the hydrogen-assisted creep fracture of hydrogen embrittled grain boundaries. Thus, the SCC growth rate is expressed as (Mohanty et al., 2012)

$$\dot{a} = \frac{r_c}{t} = \frac{r_c}{\left(\frac{\varepsilon_f}{\dot{\varepsilon}_{cfz}}\right)} = \frac{r_c \dot{\varepsilon}_{cfz}}{\varepsilon_f} \quad (46)$$

where r_c = radius of the fracture zone in front of the crack tip (mm), $\dot{\varepsilon}_{cfz}$ = strain rate in the creep fracture zone, and ε_f = critical fracture strain.

The critical fracture strain (ε_f) can be stated as (Symons, 2001)

$$\varepsilon_f = \varepsilon_{f_0} \left(\frac{C_o}{C_{gb}} \right)^{\frac{1}{2}} \quad (47)$$

where C_{gb} = grain boundary hydrogen concentration, ε_{f_0} = fracture strain at a reference grain boundary hydrogen concentration, and C_o = reference grain boundary hydrogen concentration.

Substituting Eq. (47) into Eq. (46) gives

$$\dot{a} = \frac{r_c \dot{\varepsilon}_{cfz}}{\varepsilon_{f_0}} \left(\frac{C_{gb}}{C_o} \right)^{\frac{1}{2}} \quad (48)$$

3.2.3 H₂S (sour) corrosion

H₂S corrosion of mild steel proceeds predominantly through a solid-state reaction as a result of a dense, very thin, and protective nonstoichiometric iron sulfide film formation called mackinawite (Sun and Nesic, 2006; Popoola et al., 2013). Assuming that H₂S corrosion is controlled by mass transfer resulting from the presence of mackinawite layers and the liquid boundary layer, H₂S flux through the mass transfer boundary layer is expressed as (Nešić et al., 2009)

$$J_{H_2S} = k_{m(H_2S)} (c_{H_2S} - c_{o(H_2S)}) \quad (49)$$

The flux of H₂S through the porous outer mackinawite layer is calculated as

$$J_{H_2S} = \frac{D_{H_2S} \varepsilon \psi}{\delta_{os}} (c_{o(H_2S)} - c_{i(H_2S)}) \quad (50)$$

The flux of H₂S through the inner mackinawite film is determined using

$$J_{H_2S} = A_{H_2S} \ln \left(\frac{c_{i(H_2S)}}{c_{s(H_2S)}} \right) \quad (51)$$

From Eq. (49),

$$c_{o(H_2S)} = c_{H_2S} - \frac{J_{H_2S}}{k_{m(H_2S)}} \quad (52)$$

From Eq. (50),

$$c_{o(H_2S)} = c_{i(H_2S)} + \frac{J_{H_2S} \delta_{os}}{D_{H_2S} \varepsilon \psi} \quad (53)$$

At steady state, the fluxes through different layers are equal to each other. Equating Eqs. (52) and (53) and making $c_{i(H_2S)}$ the subject, we have

$$c_{i(H_2S)} = c_{H_2S} - J_{H_2S} \left[\frac{1}{k_{m(H_2S)}} + \frac{\delta_{os}}{D_{H_2S} \varepsilon \psi} \right] \quad (54)$$

The corrosion rate caused by H₂S in metallic materials is obtained by substituting Eq. (54) into Eq. (51). Thus,

$$CR_{H_2S} = A_{H_2S} \ln \frac{c_{b,H_2S} - J_{H_2S} \left[\frac{1}{k_{m(H_2S)}} + \frac{\delta_{os}}{D_{H_2S} \varepsilon \psi} \right]}{c_{s,H_2S}} \quad (55)$$

where CR_{H_2S} = corrosion rate caused by H₂S (mol/m² s), A_{H_2S} = constant for solid-state diffusion, c_{b,H_2S} = concentration of H₂S in bulk solution (mol/m³), c_{s,H_2S} = concentration of H₂S at the steel surface (mol/m³), J_{H_2S} = flux of H₂S at different mackinawite layers (mol/m² s), $k_{m(H_2S)}$ = mass transfer coefficient of H₂S in the liquid boundary layer (m/s), δ_{os} = outer scale thickness (m), D_{H_2S} = diffusion coefficient of H₂S in water (m²/s), ε = outer mackinawite scale porosity, and ψ = outer mackinawite scale tortuosity.

3.3 OGCI adsorption isotherms

Adsorption isotherms play a key role in giving detailed information about the existing interaction between molecules of OGCI and the metal surface (Herrag et al., 2010) to prevent the dissolution reaction of such metal in the corrosive medium. Influencing factors on the adsorption process using OGCI include the (1) structure of OGCI compounds, (2) types of corrosive media under examination, (3) nature of surface-charged metals, (4) electronic characteristics of the metal surface, and (5) charge distribution in the molecules of OGCI (Vracar and Drazic, 2002; Khaled, 2010). The values obtained from the simulation of existing isotherm models relating surface coverage (θ) and OGCI concentration together describe the most suitable adsorption isotherm for the process. The prominent

OGCI adsorption isotherms have been stated to be Langmuir, Temkin, Frumkin, Freundlich, Virial Parson, and Bockris-Swinkels isotherms (Gopal et al., 2011), which are summarized in Table 7 with their verification plots and significance of obtained values. The most suitable adsorption isotherm that best describes the adsorption nature of OGCI on the examined metal surface will give a correlation coefficient (R^2) value that is very close to unity or equal to 1.

3.4 OGCI adsorption thermodynamics

The consideration of thermodynamic studies in OGCI adsorption reveals the significance of Gibbs free energy of adsorption (ΔG_{ads}^o), enthalpy of OGCI adsorption (ΔH_{ads}^o), entropy of OGCI adsorption (ΔS_{ads}^o), and apparent activation energy (E_a) of the process. The value of adsorption equilibrium constant (K_{ads}) obtained from the best-fitted isotherm tabulated in Table 8 is used to calculate ΔG_{ads}^o in Eq. (56) (Aljourani et al., 2009). The adsorption heat ΔH_{ads}^o can be calculated using van't Hoff equation in Eq. (57)

(Zhao and Mu, 1999). The entropy of OGCI adsorption ΔS_{ads}^o can be calculated using Eq. (58) (Solmaz et al., 2008). Also, the enthalpy (ΔH_a) and entropy (ΔS_a) of activation for the corrosion process can be calculated from the results obtained from temperature studies via Eq. (59) such that a plot of $\frac{\log CR}{T}$ against $\frac{1}{T}$ gives a slope of $\left(\frac{-\Delta H}{2.303R}\right)$ and intercept of $\left(\log\left(\frac{R}{nh}\right) + \frac{\Delta S}{2.303R}\right)$, which enhance the computation of ΔH_a and ΔS_a (Alaneme et al., 2016). However, many corrosion studies have shown that corrosion rate increases as temperature increases, as justified by the Arrhenius equation stated as Eq. (60) (Deyab et al., 2007). Table 8 summarizes the significance of values of thermodynamic parameters on the adsorption of OGCI on metals.

$$\Delta G_{\text{ads}}^o = -RT \ln(55.5 K_{\text{ads}}) \quad (56)$$

$$\ln K_{\text{ads}} = \left(\frac{-\Delta H_{\text{ads}}^o}{RT}\right) + \text{constant} \quad (57)$$

Table 7: OGCI adsorption isotherm models and significance of the values obtained.

Isotherm	Model	Plot	Significance of values	References
Temkin	$\theta = \left(\frac{1}{f}\right) \ln K \cdot C_{\text{OGCI Conc}}$	θ vs. $\log C_{\text{OGCI Conc}}$	If $f=0$ (no interaction), $f=+ve$ (attraction), and $f=-ve$ (repulsion) between OGCI molecules and the metal surface	Temkin and Pyzhev, 1940
Virial Parson	$\theta \cdot e^{f\theta} = K_{\text{ads}} \cdot C_{\text{OGCI Conc}}$	θ vs. $\log\left(\frac{\theta}{C_{\text{OGCI Conc}}}\right)$	1. If $f=0$ (no interaction), $f=+ve$ (attraction), and $f=-ve$ (repulsion) between OGCI molecules and the metal surface 2. If a larger value is obtained for K_{ads} ($5 \times 10^{-3} - 20 \times 10^{-3}/M$), it is an indication of a strong adsorption capacity of OGCI attributed to abundant p -electron in conjugated double or triple bonds between OGCI and vacant d -orbital of the metal specimen	Smialowska and Wieczorek, 1971
Langmuir	$\frac{\theta}{(1-\theta)} = K_{\text{ads}} \cdot C_{\text{OGCI Conc}}$	$\frac{\theta}{(1-\theta)}$ vs. $\log C_{\text{OGCI Conc}}$	A smaller K_{ads} implies a weak adsorption capacity of OGCI	Langmuir, 1947
Freundlich	$\log \theta = \log K_{\text{ads}} + n \log C_{\text{OGCI Conc}}$	$\log \theta$ vs. $\log C_{\text{OGCI Conc}}$	1. $n > 1$ implies a favorable adsorption of OGCI molecules on the metal surface. 2. A larger K_{ads} implies a strong adsorption capacity of OGCI	Piccin et al., 2011
Bockris-Swinkels	$\frac{\theta}{(1-\theta)^n} \cdot [\theta + n(1-\theta)]^{\frac{n-1}{n}} = C_{\text{OGCI Conc}} \cdot e^{\frac{-K_{\text{ads}}}{55.4}}$	$\frac{\theta}{(1-\theta)}$ vs. $\log C_{\text{OGCI Conc}}$	1. $n < 1$ implies an unfavorable adsorption of OGCI molecules on the metal surface. 2. A smaller K_{ads} implies weak adsorption capacity of OGCI	Bockris and Swinkels, 1964
Frumkin	$\left[\frac{\theta}{(1-\theta)}\right] e^{f\theta} = K_{\text{ads}} \cdot C_{\text{OGCI Conc}}$	θ vs. $\log C_{\text{OGCI Conc}}$	If $f=0$ (no interaction), $f=+ve$ (attraction), and $f=-ve$ (repulsion) between OGCI molecules and the metal surface	Trasatti, 1974

θ , Surface coverage; $C_{\text{OGCI Conc}}$, concentration of bulk OGCI (mm); f , OGCI interaction parameter; K , constant; K_{ads} , adsorption equilibrium constant ($\text{mol}^{-1} \text{dm}^3$ or M^{-1}); n , number of H_2O molecules replaced per OGCI molecule.

Table 8: Significance of values of the thermodynamic parameters on the adsorption of OGCI on metals.

Thermodynamic parameter	Significance of values on the adsorption process	References
$\Delta G_{\text{ads}}^{\circ}$	<p>If a negative value is obtained, it implies that the adsorption process is spontaneous with the formation of a stable protective OGCI layer</p> <p>$\Delta G_{\text{ads}}^{\circ} \leq -20$ kJ/mol indicates an electrostatic interaction existence between charged molecules of OGCI and charged metal. This process is called physisorption</p> <p>$\Delta G_{\text{ads}}^{\circ} \leq -40$ kJ/mol implies that there are electrons sharing or transfer from OGCI molecules to the examined metal surface to enhance the formation of a coordinate type of bond. This process is called chemisorption</p> <p>For -20 kJ/mol $\leq \Delta G_{\text{ads}}^{\circ} \leq -40$ kJ/mol, the adsorption process is a mixture between physical and chemical adsorption</p>	<p>Keleş et al., 2008</p> <p>Musa et al., 2011</p> <p>Bentiss et al., 2009</p> <p>Noor and Al-Moubaraki, 2008</p>
$\Delta H_{\text{ads}}^{\circ}$	<p>Positive $\Delta H_{\text{ads}}^{\circ}$ implies that the adsorption process is endothermic in nature; negative $\Delta H_{\text{ads}}^{\circ}$ suggests an exothermic adsorption exhibition for tested OGCI</p>	Olasehinde et al., 2013
$\Delta S_{\text{ads}}^{\circ}$	<p>Positive $\Delta S_{\text{ads}}^{\circ}$ indicates that the adsorption process of OGCI on the corroded metal surface under investigation in a corrosive medium is supported by an increase in entropy and vice versa</p>	Lazarova et al., 2009
E_a	<p>$E_a > 20$ kJ/mol suggests the inhibition process to be a controlled surface reaction</p> <p>An increase in E_a in the presence of OGCI indicates OGCI adsorption on the examined metal surface by increasing the energy barrier for the corrosion process without changing the mechanism of dissolution. Also, physical adsorption (electrostatic) has occurred at the initial stage of the process</p> <p>A decrease in E_a at higher OGCI efficiency exhibits shift in net corrosion reaction from the uncovered metal surface to the adsorbed sites</p>	<p>Herrag et al., 2010</p> <p>Khadom et al., 2010;</p> <p>Boudalia et al., 2013</p> <p>Tang et al., 2003</p>
ΔS_a	<p>An increase in ΔS_a in the presence of OGCI suggests an increase in the degree of disorderliness resulting from the conversion of reactants to activated complexes. Such exhibition could also be attributed to the reduction in the release of H^+ on the metal surface, making the system to shift from a more organized into a more random order, thereby increasing the entropy of activation</p> <p>If ΔS_a is positive, the adsorption process is enhanced by an increase in entropy, which acts as a driving force for the adsorption of OGCI on the metal surface</p> <p>Negative ΔS_a suggests the occurrence of the degree of disorderliness reduction taking place on moving from reactants to the activated states</p>	<p>Khaled and Amin, 2009</p> <p>Yurt et al., 2006</p> <p>Tang et al., 2006</p>
ΔH_a	<p>Positive ΔH_a implies that the adsorption process of OGCI on the metal surface is endothermic, whereas negative ΔH_a means exothermic reaction</p> <p>An increase in ΔH_a in the presence of OGCI suggests the presence of an energy barrier for reaction due to the adsorption of OGCI</p>	<p>Zaafarany et al., 2010</p> <p>Singh et al., 2012</p>

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T\Delta S_{\text{ads}}^{\circ} \quad (58)$$

$$\frac{\log CR}{T} = \log \left(\frac{R}{Nh} \right) + \frac{\Delta S_a}{2.303R} - \frac{\Delta H_a}{2.303RT} \quad (59)$$

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (60)$$

where CR = corrosion rate (mm/year), N = Avogadro's number (6.02×10^{23} /mol), h = Plank's constant (6.63×10^{-34} m² kg/s), R = gas constant (8314 J/mol K), T = absolute temperature (K), E_a = activation energy (kJ/mol), and A = pre-exponential factor.

4 Conclusions and recommendations

- Many of the greeners considered for the extraction of OGCI are edible and very useful for human need in many areas such as medicinal, pharmaceutical, and food consumption, thus making them to be very competitive in terms of functionality. There is a need for future research works to focus more on wastes from greeners constituting environmental nuisance causing harmful effects on both human and aquatic natures. Recently, Al-Zubaidi et al. (2018) used crude glycerol (by-product of biodiesel production) with a concentration range from 0.1% to 1.0% (w/w) as a potential OGCI for steel corrosion in a corrosive

medium containing 0.5 M HCl at a constant room temperature of 25°C.

2. It has been established that many silicates also possess corrosion inhibitory attributes due to their capability to block corrosion active sites on metals in acidic medium. Researchers should focus on synthesizing composite OGCI from greener extracts and silicates (such as rice husk waste) to improve their efficiency. This phenomenon is referred to as a synergism effect, which can be quantified by applying Eq. (7). This will also enable researchers to widen their scope and knowledge of using naturally endowed greeners.
3. None of the examined studies presented chain reaction mechanisms and reaction pathways showing the presence of intermediates in the course of corrosion reaction inhibitory effects of used OGCI and examined metals. This is necessary to know how these intermediates contribute or affect the inhibition via the adsorption of OGCI on metals. It is an established fact that when extracts from greeners react, intermediates are formed in the course.
4. Also, there is a complexity of adequate separation techniques to be employed in obtaining tested acidic or alkaline solution (as the case may be) in pure form and the spent OGCI. The reusability of spent OGCI, and decrease in their efficiency over time, is a great challenge for prospective researchers in the field of corrosion engineering.
5. Cost-effective modern techniques that will also maximize OGCI extraction in pure form from their sources are required. A detailed financial implication from pilot scale to full industrial plant is needed for the general public to see this as a key means of internal revenue generation. Previous studies focused majorly on refluxing greeners in HCl, ethanol, and H_2SO_4 for a period of time. In support of these, existing optimization tools such as response surface methodology and central composite design of design experts coupled with predictive tools such as artificial neural network-based Monte Carlo simulation and sum of square errors will be of help (Popoola and Susu, 2014).
6. The gap between research and industrial application of these OGCI has not been bridged. From investigation, many industries are still using corrosion inhibitors already in existence, which have been proven to be expensive and environmental unfriendly although researchers are working assiduously to generate cheap, environment friendly, and readily available OGCI from greeners. Researchers' efforts should be appreciated in this regard.
7. In the examined functional groups presented in Table 2, flavonoid has been observed to be a peculiar active corrosion inhibition constituent present in almost 85% of the greeners presented. Flavonoid is a good candidate to explain the corrosion inhibitory effects observed in greeners. Its detailed chemistry must be studied to enhance further works on the contribution of flavonoid in OGCI on the corrosion inhibition of metals.
8. Phytochemical analysis provides information on active ingredients present in plant extracts acting as corrosion inhibitors of OGCI. Therefore, it is most likely that a mixture of constituents is acting as corrosion inhibitors (Raja and Sethuraman, 2008). Few studies are engaged in using this analysis.
9. Additional advanced characterization techniques coupled with fundamental studies are required to further differentiate OGCI mechanism and investigate the relationship binding their structure with experienced corrosion inhibition. This knowledge will help tailor the OGCI structure in obtaining the necessary corrosion inhibitory properties (Taghavikish et al., 2017).
10. Although synthetic inhibitors have been shown to be expensive and toxic with restrictive environmental regulations in many countries, they have high corrosion inhibitory effectiveness. However, OGCI from plant extracts with biodegradability, nontoxic, and environment friendly potential exhibit low corrosion inhibition efficiency as presented in many studies (Finšgar and Jackson, 2014). Due to this point, further research works are required on using additives such as water wetting agents, iron control agents, viscoelastic surfactants, nonemulsifiers, antisludge agents, and stabilizers to green corrosion inhibitors. They do not have corrosion inhibition potential but can enhance the corrosion inhibition performance of OGCI and significantly reduce the corrosion rate.
11. Although many studies suggested Langmuir as the best predictive adsorption isotherm that conforms to experimental data, further studies are required for the kinetics of the corrosion inhibition of materials by OGCI via the previously presented modeling equations. Also, more studies are needed in the aspect of developing mathematical models with reduced assumptions involving kinetics and mechanistic studies in predicting the corrosion inhibitory effects of OGCI from plant extracts. Computer software that will enhance quick prediction and other applications pertaining to corrosion inhibition exhibits of these OGCI can be developed.

12. It has been established that organic compound structures of OGCI play a vital role on how they effectively inhibit the corrosion of metal. This means that changing the organic compound chemical structure will directly sectionize corrosion inhibition. This calls for advanced research works in the development of quantitative models bridging chemical structure to properties using existing machine learning or statistical approaches. Although quantitative structure-activity relationships and quantitative structure-property relationships modeling have been presented (Winkler and Burden, 2000; Le et al., 2012; Fujita and Winkler, 2016), there is a need for more machine learning modeling methods and computational models that are applicable in studying the corrosion inhibitory properties of OGCI organic compounds. Also, improvements in robotics and machine learning will pave ways to tremendous increase in the efficiencies and dependency of methods for designing OGCI within a short period.
13. The corrosion inhibitory effects of OGCI on mild steel have been the major consideration in numerous previous studies because of its relatively low price with acceptable material properties for many domestic and industrial applications (Singh et al., 2016). However, its low corrosion resistance in acidic environments is a major challenge (Alaneme et al., 2016). There is a need to work assiduously on other metallic components such as copper, alloys, aluminum, and stainless steel.
- All these work in unison and play specific roles in material selection for domestic/industrial purposes. They also corrode when subjected to certain environmental conditions. They are also the major components of automobiles, whose major concern is corrosion.
14. Building collapse has been linked majorly to the weakening of iron steel rods (used in concrete beams) as a result of corrosion over a period of time. Thorough research is required on the use of OGCI from greeners that have strong affinity for concrete cements and constituents (pastes) to increase the life span of reinforced concrete structures damaged as a result of high alkalinity and tackle rusting of these iron rods used in building construction.
15. Some corrosion inhibitors extracted from *Ginkgo biloba* leaf (Chen et al., 2013) and *Diospyros kaki* L.f husk (Zhang et al., 2013) that have exhibited potential for corrosion inhibition for microbial-induced corrosion type need to be further investigated for other forms of corrosion to widen the scope of corrosion control in the oil and gas industries. More research should be carried out on other corrosive environments such as CO₂, H₂S, and NaCl with great impact on metals used in the oil and gas industries. Nevertheless, the identification of corrosion type inhibited by OGCI based on the solution examined for the materials is necessary.
16. Acid solutions have found industrial application in mill scale removal from metal surfaces, acid descaling,

Table 9: Employed methodologies to reduce corrosion examination time.

Materials	Methodologies	No. of inhibitors	Observation period	Observation(s)	References
Al alloy (AA2024)	Direct current polarization	50	9 h	Results obtained correlated perfectly with those with 10 days of extended testing period	Chambers et al., 2005
Al ³⁺	Fluorometric detection	14	1–7 days	Excellent results obtained with high accuracy within a limited period	Chambers and Taylor, 2007
Al ³⁺	Direct current polarization, cyclic voltammetry, and fluorometric detection	100	3–5 days	Better results with high accuracy within a short period	Taylor and Chambers, 2008
Fe and Zn	Scanning vibrating electrode technique	4	≈2 h	Accurate determination of percent corrosion inhibition efficiencies	Kallip et al., 2010
Carbon steel	High-throughput testing rig	88	≈1 day	Best ever methodology that can handle many inhibitors within a short period on a single plate with negative and positive controls	White et al., 2012
Mild steel	High-throughput EIS	12	≈3 h	An electrochemical platform with spatially addressable feature interfaced to a commercial EIS instrument was developed	He et al., 2008
Mild steel	Robust computerized optical image processing method	25	≈2 h	A linear relationship binding image apparent grayscale value with a corrosive pitting depth in the specimens was revealed	Villamizar et al., 2006

acid pickling, industrial acid cleaning, and oil well acidizing. An important stimulation technique for enhancing oil production is petroleum oil well acidification. However, studies of metal corrosion using organic acid solutions are rare compared to similar studies with mineral acids as corrosive media (Sekine et al., 1987). Among acid solutions, HCl and H_2SO_4 are the most widely used because of their high corrosive nature to most metals and alloys even at low concentrations (Bekkouch et al., 1999), whereas HNO_3 and H_3PO_4 are explored in isolated cases (El-Din, 2009). It is very important to put these mineral acids and organic acids into consideration during the corrosion inhibition of metals using OGCI as they are among the highly ranked important industrial chemicals.

17. Previous researchers have been using days and months to critically figure out the adsorption corrosion process of examined materials, media (either acidic or alkaline), and inhibitors from greeners to truly determine the percent inhibition efficiency of inhibitors. Although very few researchers have been working on methodologies and technologies to reduce the corrosion examination period as presented in Table 9, there is still a need for thorough research works by many researchers on novel methodologies that can examine hundreds or thousands of materials within a few minutes with optimum accuracy of inhibition efficiency determination. The most common methodologies that have been employed and adopted are EIS, WLM, and PDP.

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