Recent Advances in Green Inhibitors as Anticorrosion Agent for Aluminium and Its Alloys in Various Corrosive Media: A Review

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Abstract: Metal corrosion is a natural process caused by environmental factors such as moisture, oxygen and chemicals. This review explores Aluminium (Al) corrosion protection in acidic and alkaline media, focusing on eco-friendly green inhibitors derived from natural sources like plant extracts, organic and biopolymers. A protective thin film layer formed by the chemical adsorption of the inhibitor or by the combination of inhibitor ions with the metal surface in the corrosion of aluminium. Various analytical techniques used to assess inhibition efficiency and surface properties including Gravimetric (weight loss), Temperature effect, Gasometric, Potentiodynamic polarization, Hydrogen evaluation and Electrochemical impedance spectroscopy, Surface analytical methods include Scanning electron microscopy, Response surface methodology, Energy dispersive X-ray spectroscopy, Atomic force microscopy, Fukui functions, X-ray diffraction, X-ray fluorescence and Electrochemical frequency modulation. Absorbed inhibitor molecules contains functional groups analyzed by Ultraviolet-visible spectroscopy, Fourier transform infrared spectroscopy, Gas chromatography, Liquid chromatography and Mass spectrometry. Computational studies include Density functional theory study of electronic structure and interactions and Molecular dynamics simulation predict insights into the dynamic behavior of atoms and molecules. These techniques help to understand the properties of protective coatings, contributing to corrosion prevention, material durability and industrial applications. Overall, this review provides a comprehensive overview of recently studied various green inhibitors for aluminium corrosion protection in different corrosive environments.

Keywords: Aluminium, Corrosion, Green Inhibitor, PDP, EIS, SEM, FTIR, DFT, Molecular Dynamics Simulation.

1. Introduction

Corrosion occurs when a refined metal undergoes a natural transformation into a more stable form such as its oxide, hydroxide or sulfide state, resulting in the deterioration of the material. Aluminium as a widely used material due to its lightweight nature, silvery-white appearance. Aluminium ranks as the third most abundant element and the most lavish metal in the earth's crust, comprising approximately 8.0 % of total mineral elements[1]. Aluminium is commonly used in various industries due to its versatility, conductivity and malleability. Aluminium used in electronics due to its super purity[2]. It often used in the production of including aerospace[3], automobiles, packaging materials and construction materials. Some of them include pickling[4], anodizing (surface treatments)[5] and metal-metal cleaning/descaling which involves the use of acidic solutions, alkaline solutions, alcohols, water, etc. In terms of corrosion, aluminium lacks inherent resistance on its own. However, when an oxide layer forms on its surface, aluminium becomes highly resistant to corrosion in various environments[6, 7]. This oxide layer acts as a protective barrier, preventing further metal deposition. Nevertheless, when exposed to corrosive media, this oxide layer can become damaged, leaving the metal surface vulnerable to the corrosive environment's attack[8, 6].

There were various methods to prevent corrosion show in figure 1, which decreased the rate of corrosion and increase the lifetime of metals and its alloy. Inhibitors were commonly used to prevent or reduce metal corrosion by forming a protective layer on the metal surface. These were used in lower concentration in corrosive media and successfully reduces the deterioration of a metal exposed to the corrosive environment[9, 10]. These inhibitors function either by adsorbing onto the surface of metal to prevent corrosive agents from reaching it or by modifying the electrochemical reactions that cause corrosion[11]. Different types of inhibitors including organic, inorganic and green

or natural compounds used for prevention of metal corrosion, which were often used to coatings, paints or directly applied on the surface of metal[12]. The organic inhibitor compounds were applied in acidic medium, while inorganic inhibitors in the alkaline medium[13, 7].

Figure 1. Commonly used methods for prevention and control of metal corrosion.

Nowadays, Green inhibitors required for corrosion prevention because they are environmentally friendly and sustainable characteristics. Unlike traditional inhibitors, green inhibitors are derived from natural sources or biodegradable, making them less harmful to the environment. Conventional inhibitors that is not only expensive but also toxic in nature and non-biodegradable which cause to create pollution[14, 8]. Using green inhibitors aligns with the principles of sustainable development and reduces the overall environmental impact of corrosion prevention practices. They are thermally stable, chemically inert, low cost and easily available, it shows good inhibition effectiveness at very low concentration[15, 9]. The corrosion inhibitors that have been in high demand are those that satisfy the conditions illustrated in the figure 2.

Green inhibitors are equally effective as traditional inhibitors in preventing corrosion on metal surfaces. This is highlight their potential as sustainable alternatives in corrosion prevention practices, aligning with the growing emphasis on environmental responsibility in various industries[16]. Natural product contains essential elements like O, N and S as heteroatoms and electron-donating groups. The order of inhibition efficiency should be $P > S > N > O$[10]. Researchers aim to explore the active components in organic compounds aid in the adsorption onto aluminium or its alloys, forming a protective film that impedes corrosion. Their focus on investigating the corrosion inhibition of aluminium and its alloys using different plant extracts[16]. This report summarizes recent research on plant and other inhibitor extracts as eco-friendly corrosion inhibitors, examines the fundamental methods used to evaluate inhibition effectiveness and notes the various techniques documented in the literature. The discussion highlights the challenges and potential future developments for the broader application of green inhibitors.
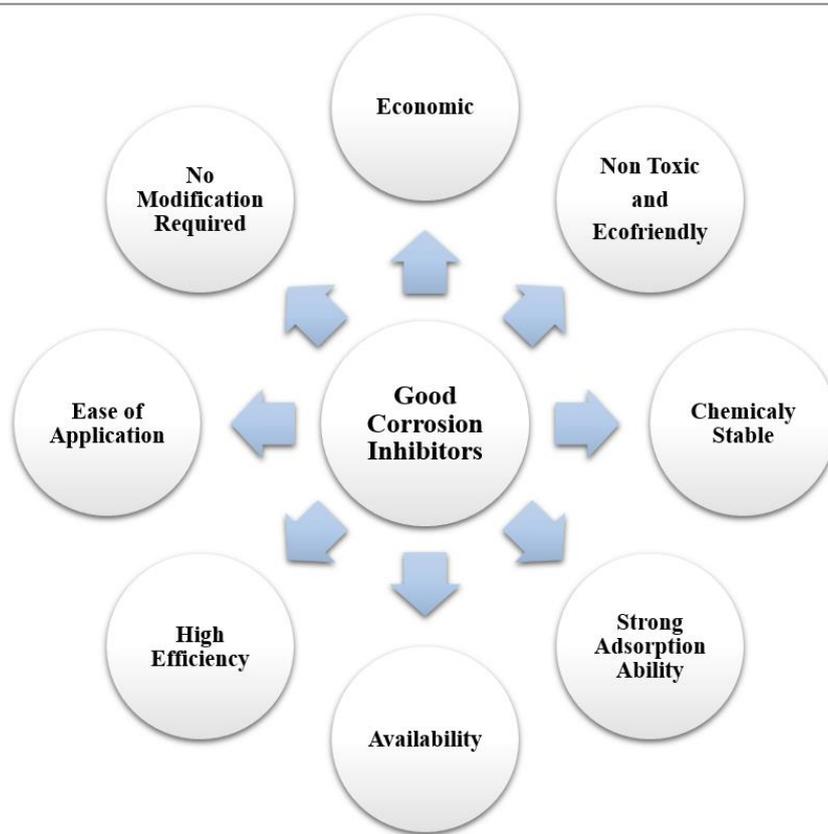
Figure 2. Expected qualities of an effective corrosion inhibitor.

2. Experimental

2.1 Corrosive medium

This review explores the use of organic, green and biopolymer inhibitors to prevent aluminium corrosion in acidic and alkaline environments. Specifically, it investigates the effectiveness of certain plant extracts as green inhibitors for corrosion control in both acidic and alkaline conditions such as HCl[17, 18, 20, 21, 23, 24, 27, 29, 33, 36, 37, 40-42, 44, 47 to 49, 52, 54-56, 58, 59, 62, 66-71, 74-81], NaOH[18, 22, 26, 28, 36], H_2SO_4[19, 27, 32, 35, 37, 43, 44, 46, 50, 53, 57, 64, 65], H_3PO_4[19], NaCl[25, 31, 34, 38, 51, 61, 64], KOH[26, 63], Sea water[39], HNO_3[45, 82], H_3PO_4[30] and Gasoline[73].

2.2 Green inhibitors and additives

Plant extracts of various parts of the plant like, Leaves[17, 21, 22, 25, 36, 37, 40, 41, 43, 46, 47, 49, 52, 53, 55, 56, 60, 63], Fruit[18, 44, 49, 79], Fruit Peels[19, 68, 77, 81, 82], Stem/Stalk/Straw[19, 23, 44, 49, 55, 58, 74], Aerial Part[20, 39], Plant[26, 33, 65], Shell[31,32, 35, 48, 57] Bulb[30, 34], Flower[38, 71, 78], Root[44], Bark[44], Weed[45], Seeds[50, 51, 57, 59, 66, 67], Seed oil[69] and Sap[74] were used. In some cases, additives such as KCl, KBr, 4-pyridinecarboxaldehyde, TiO_2[31], 3% Nacl[40], $NaKC_4H_4O_6 \cdot 4H_2O$[61] and Na_2SiO_3[72] used with green inhibitor to understand their synergic effect.

2.3 Metal

Different grades of aluminium were used to recognise corrosion behavior, such as Al-alloy AA8011[17], Al[18-21, 23, 24, 26, 28, 29, 30, 33, 36, 37, 43-45, 49, 55, 59, 63, 65-69, 71, 73-80], Al-alloy[22,27], Al-alloy AA7075-T7351[25], Al-alloy C3003[31], Al-alloy AA5052[32], Al-1050[34, 82], Al-99.99%[35], Al-carbon fibered based coated[38], Al-alloy 5083[39], Al-alloy 1060[45, 58], Al-alloy AA2024-T3[48, 72], Al-99.999%[50], Al-alloy 2024T3[51], Al-alloy 1060[52], Al-alloy 1100[53], Al-alloy 7075[54], Al-alloy AA7051[60], Al-alloy GOST 4784-97[61], Al-alloy 99.98%[62], Al-alloy AA1070[64] and Al-alloy AA303[70].

2.4 Aqueous extraction solvent

The plant materials have been prepared by extracting use of Methanol[17, 43, 62, 67, 68, 73], Water[18, 24, 26, 28, 30, 41, 38, 51, 53, 56, 60, 66, 71, 74, 75], Ethanol[19-21, 23, 36, 42, 44-48, 52, 58, 59, 72, 76, 80, 82], Ethanol-Water[25, 33, 81], Acetone[37], Alcohol[55] and Dichloromethan[77, 78, 79].

2.5 Temperature effect

The inhibition efficiency has been studied at room temperature[20, 22, 31, 34, 35, 38- 40, 44, 46, 48-50, 53, 55, 59, 61, 64, 66, 70, 72- 74] and at various temperature[17-19, 21, 23-30, 32, 33, 36, 37, 41-43, 45, 47, 51, 52, 56, 58, 60, 62, 63, 65, 67-69, 71, 75-79, 81-82].

2.6 Methods

Green inhibitors were introduced into corrosive environment to protect metal corrosion by forming a protective film on the metal surface. This film's efficacy confirmed through surface morphological studies such as Gravimetric Analysis (Weight/Mass loss)[17, 18, 20-29, 32, 33, 35-38, 40, 41, 43-53, 55-58, 62-64, 65-82], Kinetic paramters[33, 67, 71, 86, 88], Fourier transform infrared spectroscopy (FT-IR)[18, 19, 21-23, 26, 31, 37-39, 51, 53, 54, 56, 70, 72, 73, 75, 76, 81, 82], Scanning electron microscopy (SEM)[19, 21, 22, 25-27, 29-32, 33, 35, 36, 38, 42, 45, 49, 51-54, 57, 61, 62, 65, 66, 73, 76-78, 80, 82], Atomic force microscopy (AFM)[19, 23, 31, 45, 54, 65, 72, 77-79, 82], Gas Chromatography (GC)[19, 73, 74, 82], Liquid Chromatography (LC)[33], Mass Spectrometry[19, 33, 73, 74, 82], Linear Polarization Resistance (LPR)[21, 73], Potential dynamic polarization (PDP)[19-24, 27, 30-36, 38, 39, 41, 42, 48, 50-53, 59, 64, 65, 66, 68, 72, 75, 77-80, 82], Polarization[26, 37, 49, 60-62], Open Circuit Potential (OCP)[20, 31, 37, 64, 65, 71], Electrochemical impedance spectroscopy (EIS)[20-24, 26-31, 33, 34, 37-39, 41, 45, 48-50, 52, 61, 62, 65, 66, 68, 70, 72-75, 77-79, 82], X-Ray Photoelectron Spectroscopy (XPS)[23, 33, 45, 65, 68, 72], X-ray Diffraction spectroscopy (XRD)[31, 53, 64], X-ray fluorescence (XRF)[57, 64], Electrochemical noise analysis[34], UV Spectroscopy[33, 37, 54, 80], Contact Angle[37, 54], Cyclic Voltammetry[39], Attenuated Total Reflection (ATR) Spectra[52], Gasometric[55], Hydrogen Evolution[50, 55], Density functional theory (DFT)[37, 54], Fukui functions(FFs)[62], Molecular dynamics-Monte Carlo simulation[62], Optical microscopy characterization(OCM)[64], Response surface methodology(RSM)[70], Quantum chemical[72, 82] and Electrochemical noise (EN)[73] were used to investigate the corrosion behavior and to find inhibition efficiency of different organic and green inhibitors.

2.7 Adsorption isotherms

The adsorption isotherm for phytochemical constituents present in green inhibitors extract into the metallic surface has been studied by various types of adsorption isotherms such as, Langmuir[17, 18, 21, 23-26, 33, 35, 36, 38, 39, 40, 42-50, 52, 54, 56, 58, 60, 62, 65, 67-71, 73, 74, 77-81], Flory Huggins[21, 23, 36, 43, 45, 69], Freundlich[17, 21, 25, 33, 40, 43, 45, 47, 49, 74, 81] and Temkin adsorption[17, 21, 25, 26, 36, 40, 42, 43, 45, 47, 49, 52, 69, 74], Dubinin-Radushkevich[17], Villamil[17], El-Awady[17, 21, 43, 45], Virial Parson[43] and Frumkin[69,74] isotherm.

2.8 Active phytochemicals found in green inhibitors

Green plant extract shows good potential corrosion inhibition for aluminium in acidic, alkaline or neutral corrosive medium. The green inhibitors contains various active phyto-chemical constituents vary among different plant breeds but their chemical structures were closely related to their organic compounds, e.g. *Rosmarinus Officinalis*[17] contains rosmarinic acid, carnosic acid and carnosol. Apple peel contains flavonoids like quercetin glycosides and Grape stems contains resveratrol, flavonoids, anthocyanins and tannins[18]. The primary chemical constituents such are flavone extracts from apple peel and aldehydes from grape stems[19]. *Artemisia herba alba*[20] contains chrysanthenone (24.10%), camphor (16.20%), α-thujone (12.80%), 1,8-cineole (9.30%) and β-thujone (4.80%), camphene, sabinene and α-pinene present by chromatographic analysis. Phytochemical screening of *Guiera senegalensis*[21] leaf extract contains kaempferol, ethylgallate, gallic acid, 5-methylflavasperone, 5-methyldihydroflavasperone, guieranone, quercitrin. β-sitosterol, 1,3,4-tri-O-galloilquinic acid, 3,4,5-tri-O-galloilquinic acid, miricitrin, rhamnetin, hyperoside, miricetin, quercetin, tilir tiliroside and isorhamnetin, act as adsorption on the aluminium surface to inhibit corrosion. *Syzygium samarangense*[22] leaf extract contains ursolic aldehyde, betulin, betulinic acid and various chalcones. Rice straw[23] extract acts as an eco-friendly inhibitor, primarily through the adsorption of organic constituents like lignin, cellulose, ash and hemicellulose. *Ilex paraguariensis*[24] contains phenolic compound, polyphenols (chlorogenic acid) and xanthines (caffeine, theobromine and theophylline), as per purine alkaloids (4,5-dicaphoxyquinic acid, 3,4-dicaffeoylquinic acid, 3,5-dicaffeoylquinic acid), flavonoids (quercetin, kaempferol and rutin), amino acids and saponins, minerals (P, Fe and Ca) and vitamins (C, B$_1$ and B$_2$) in extract. *Treculia africana*[25] leaves extract with its inhibiting properties attributed to its biologically active due to presence of flavonoids, saponins and polyphenols. *Aspilia mossambicensis* and *Emilia sonchifolia* extracts is driven by the adsorption of organic compounds, including alkaloids, flavonoids, tannins and terpenoids[26]. Flavonoids, saponins, tannins, alkaloids and steroids as phytochemicals in *Justicia secunda* leaves[27]. The *Derris indica*[28] extract's phytochemicals, including flavonoids, alkaloids, tannins and phenols. *Dogonyaro* leaf[29] extract contains phytochemical constituents such as saponins,

alkaloids, flavonoids, glycosides and terpenoids as active corrosion-inhibiting agents. *Alternanthera philoxeroides*[33] contains indole, L-kynurenine, cinnamic acid, 5-hydroxyindoleacetic acid and citrate. Molecules such as allicin, alliin, pyridoxal phosphate and pyrrole, derived from garlic extract[34]. *Vitellaria paradoxa*[36] extract contains saponins, tannins, alkaloids and flavonoids. *Lippia javanica*[37] leaf extract contains Verbascoside (Acteoside) identified as a major constituent with multiple phenolic hydroxyl groups. *Artemisia annua l.*[39] extract to identify chlorogenic acid and caffeic acid as the primary phytochemicals. *Irvingia gabonensis*[40] contains several organic compounds having hetero atoms with high molecular weight such as saponin, alkaloids, tannins, flavonoid and phenol. *Capparis decidua*[44] extract contains alkaloids (capparisinine), flavonoids and tannins.

As per liquid chromatography and mass spectrometry analysis, phenolic acids, fatty acids, flavonoids, amino acids, nucleotides or 4-Hydroxybenzoic acid, protocatechuic acid, p-coumaric acid, vanillin, kaempferol-3-O-rutinoside, isoquercitrin and astragalin were present in *Mikania micrantha*[45]. Irish potato[46] (*Solanum tuberosum*) leaf extract contains phytochemical in the referenced study identifies starch and saponins, tannins, alkaloids, flavonoids and phenols as the primary active components. *Irvingia gabonensis*[47] extract, identifies alkaloids, flavonoids, tannins and saponins as the specific phytochemicals. Saponins, glycosides, flavonoids, tannins and alkaloids as the key phytochemicals in the alcoholic extract of *Tribulus terrestris* aerial parts[49]. Saturated Fatty acids such as oleic acid, linoleic acid were present in Almond oil[50]. Basil seeds[51] belonging to the lamiaceaes family, contains many compounds phytochemicals such as plantose, mucilage, polysaccharides and carbohydrate, fats, protein and α-linolenic acid. *Ziziphus spina-christi*[52] identifies betulinic acid, quercetin and cyclopeptide alkaloids as phytochemicals. *Cichorium intybus* seeds[54] extract, identifies cichoric acid, chlorogenic acid and esculetin as phytochemicals. Sunflower stalk extract contains chlorogenic acid, caffeic acid and quercetin[58]. Guar gum[61] as a natural polymer, a base formed by monomeric units of D-mannopyranose connected with each other through β-bond and a side branch with one α-D-galactopyranose connected with a mannose unit via α-bond present in extract. Myrrh[62] Extract contains α-pinene, β-pinene, limonene, myrcene, curzerene, furanoeudesma-1,3-diene and β-elemene, furanoeudesma-1,3-dien, lindestrene, and furanodiene. The extract of grape leaf[63] extract contains alkaloids, flavonoids, saponins, tannins, steroids and glycosides. *Hemerocallis fulva* extract contains chlorogenic acid, quercetin and rutin[65].

Cuminum Cyminum (Jeeru) seeds extract contains 2-3 % essential oil, 22 % fatty oil, 18 % protein, 14 free amino acids, flavonoids, glycosides, tannins, resins and gum and primary constituents are cuminaldehyde, p-cymene and terpenoid[66]. Fennel[67] seeds extract contains α-pinene, β-myrcene, β-pinene, bitter fenchone, camphene, estragole (methylchavicol), fenchone, limonene, p-cymene and safrole. Linoleic acid, palmitic acid and stigmasterol found in pumpkin peel extract[68]. *Ricinus communis*[69] extract contained phytochemicals of alkaloids, cardiac glycosides, flavonoids, phenolics, phytates, saponins and tanins. Phytochemical analysis of *Sapium ellipticum* leaf[70] extract identifies tannins, flavonoids, triterpenoids and alkaloids. The Rose leaves extract contains anthocyanins, flavonoids (quercetin, kaempferol), tannins, phenolic acids and essential oils (citronellol, geraniol). Rose flower[71] extract contains eugenol, geraniol, citral (3, 7-dimethylocta-2, 6-dienal) and citronellol, (3,7-dimethyl-6-en-1-ol). *Annona muricata* leaf extract contains a potent mix of annonaceous acetogenins such as annonacin and bullatacin, alkaloids, flavonoids and tannins[72]. The primary components identified in *Annona muricata*[73] extract include EDL-arabinose, 1-pentanol, 2-methyl-acetate, folic Acid, R-limonene, dodecanoic acid, 2-hexyl methyl ester, vitamin E, among others are volatile phytochemicals of *Musa Paradisiaca Stem Sap*[74] contains phthalic acid, pentadecyl 2-propylphenyl ester, eicosane, 2-methyltetracosane, octacosane, tetrapentacontane, octadecane, tetrapentacontane, etc. The main components polyphenols, flavonoids, carotenoids, alkaloids, quercetin, kaempferol, apigenin detected in the *Moringa oleifera* extract[75].

The leaf extract of *Lagenaria breviflora*[76] contains tannins, diterpenes, sterols, flavonoids, cardiac glycosides and phenols. Sweet orange peels[77] contains flavonoid compounds, steroids, terpenoids, alkanes and ethyl esters. The primary chemical constituents of yellow oleander[78] include thevetin B, cannogenin, digoxigenin and cannonigenol. The main constituents of the *Xanthium spinosum* fruit[79] include germacrene D, eudesma-4 (14), 7-dien-1 β-ol, spathulenol and cadalene. Phenolic compounds and flavonoids were commonly present in *Hibiscus sabdariffa* leaf extracts and Identified constituents in the *Hibiscus sabdariffa* leaf[80] extract include hydroxycinnamates, anthocyanins, delphinidin, cyaniding, etc. The efficacy of red onion skin[81] extract as an environment friendly inhibitor attributed to its high content of flavonoids, polyphenols, quercetin and other organic compounds. 17-Octadecynoic acid, 1-β-d-

Ribofuranosy l-3-, Hexanoic acid, 4-methyl, 3-Butyl-4-nitro-pent-4-enoic acid, methyl ester, etc. and 5-hydroxymethylfurfural the main substance compounds present in pomegranate peel extract[82]. The list of various types of green inhibitors used to protect aluminium from corrosion in different corrosive environments shown in table 1.

Table 1: Green inhibitors for aluminium and its alloy in different corrosive medium.

Sr. No.	Metal and Corrosive media	Inhibitor	Part of Plant	Additive	Methods	Finding	Inhibition Efficiency	Ref.
1	Al (0.25M HCl)	*Rosmarinus officinalis l.* (Rosemary)	Leaves	-	Weight loss	Langmuir adsorption, Villamil, Freundlich, Temkin, El-Awady, Dubinin-Radush-kevich isotherm	68.68%	17
2	Al (1.0M HCl and NaOH)	*Acacia nilotica*	Fruit	-	Weight loss and FTIR	Langmuir adsorption isotherm	98.83 and 71.64%	18
3	Al (60% H_3PO_4: 40% H_2SO_4)	Apple peel and Grape stems	Peel and Stems	-	SEM, AFM, FTIR, UV Spectroscopy, GC-MS and Polarization	-	92.07%	19
4	Al (1.0M HCl)	*Artemisia herba-alba*	Aerial parts	-	Weight loss, OCP, Polarization and EIS	-	94.30%	20
5	Al (0.2M HCl)	*Guiera senegalensis*	Leaves	-	LPR, FTIR and SEM	Flory Huggins, Langmuir, Freundlich, Temkin and El-awady isotherm	65.71%	21
6	Al (NaOH)	*Syzygium samaragense*	Leaves	-	Weight loss, Polarization, EIS, FTIR and SEM	-	-	22
7	Al (2.0M HCl)	Rice straw	Straw	-	Mass loss, EIS, FTIR, XPS, AFM and Polarization	Flory Huggins and Langmuir isotherms	96.8%	23
8	Al (0.1M HCl)	*Ilex paraguar-iensis* (Yerba mate)	-	-	Weight loss, EIS and Polarization	Langmuir isotherm	71.00%	24

9	Al (2.86% NaCl)	*Treculia africana*	Leaves	-	Weight loss and SEM	Langmuir, Freundlich and Temkin	91.00%	25
10	Al (1.0M NaOH and KOH)	*Aspilia mossamb-icensis* and *Emilia sonchifolia*	Leaves	-	Gravimetric, polarization, EIS, FTIR, SEM and Polarization	Langmuir, Temkin isotherm and Gibbs free energy	79.04% and 77.00%	26
11	Al (0.5M HCl)	*Justicia secunda*	Leaves	-	Weight loss, EIS, PDP and SEM	-	94.30%	27
12	Al (1M NaOH)	*Derris indica*	Leaves	-	Weight loss, PDP and EIS	-	60.20%	28
13	Al (0.3M HCl)	*Dogonyaro*	Leaves	-	Weight loss, EIS and SEM	-	99.46%	29
14	Al (Vynil trietoxy silane coated) (0.05 M H_3PO_4)	Garlic	Bulb	-	Temperature effect, Polarization and EIS	-	90.00 %	30
15	Al-alloy (3.5% NaCl)	Chitosan	Shells	4-Pyridinecarb oxaldehyde, TiO_2	AFM, FTIR, EIS, XRD, SEM, EDS, OCP and PDP	Tafel analysis	94.5 %	31
16	Al (0.5M H_2SO_4)	Chitosan	Shells	-	Weight loss, SEM, EDX and Polarization	Activation energy analysis	95.12%	32
17	Al (1.0M HCl)	*Alternan-thera philoxero-ides*	Plant	-	Weight loss, Kinetic study, EIS, SEM, XPS, LC-MS and UV Spectroscopy	Langmuir and Freundlich adsorption isotherm	92.00% mixed-type inhibitor	33
18	Al (3.5% NaCl)	Garlic	Bulbs	-	Polarization, EIS and EN	Molecular dynamics simulation	80.70%	34
19	Al (0.5M H_2SO_4)	Coconut shell	Shells	-	Gravimetric, SEM, EDX and PDP	Langmuir adsorption	99.00%	35
20	Al (0.6M HCl and NaOH)	*Vitellaria paradoxa*	Leaves	-	Weight Loss, SEM, EDX and Polarization	Langmuir, Flory-Huggins and Temkin isotherm	56.34%	36

21	Al (1.0M HCl)	*Lippia Javanica*	Leaves	-	Gravimetric analysis, EIS, LPR, UV Spectroscopy, FTIR, OCP and Contact angle	DFT	91.89%	37
22	Al-Carbon fibre laminate (3.5% NaCl)	*Aerva lanata*	Flower	-	Weight loss, PDP, FTIR, EIS and SEM	Langmuir adsorption isotherm	92.00%	38
23	Al (Sea-water)	*Artemisia annua l.* (Sweet wormwood)	Aerial parts of stem	-	Cyclic voltammetry, Polarization and EIS	Langmuir adsorption isotherm and FTIR	78.60%	39
24	Al (0.01M HCl)	*Irvingia gabonensis*	Leaves	3% NaCl	Gravimetric analysis	Langmuir, Freundlich and Temkin Isotherm	67.00%	40
25	Al (3.0M HCl)	*T. Conophorum*	Leaves	-	Weight loss, PDP and EIS	-	78.63%	41
26	Al (1.0M HCl)	*Capparis decidua*	Plant	-	Mass loss, SEM and PDP	Langmuir adsorption and Temkin isotherm	88.20%	42
27	Al (0.5M H_2SO_4)	Caesar weed	Leaves	-	Weight loss	Frumkin, Temkin, Henry, Freundlich, Langmuir, El-Awady, Virial Parson and Flory huggins	80.00 to 85.00%	43
28	Al (0.5N HCl and 0.5N H_2SO_4)	*Capparis decidua*	Fruit, Root, Stem and Bark	-	Weight loss	Langmuir adsorption isotherm	98.73%	44
29	Al (0.1M HNO_3)	*Mikania micrantha*	Weed	-	Weight loss, EIS, XPS, SEM and AFM	Flory huggins, Langmuir, Freundlich, Temkin and El-Awady isotherm	97.6%	45

30	Al (2.0M H_2SO_4)	Irish potato (*Solamun tuberosum*)	Leaves	-	Weight Loss	Langmuir adsorption isotherm	77.78%	46
31	Al (1.0M HCl)	*Irvingia-gabonensis*	Leaves	-	Weight loss	Langmuir, Freundlich and Temkin isotherm	98.00%	47
32	Al (1.0M HCl)	Coconut shell	Shell	-	Weight loss, PDP and EIS	Langmuir adsorption isotherm	97.91%	48
33	Al (1.0M HCl)	*Tribulus terrestris* plant	Fruit, Leaves and Stem	-	Mass loss, SEM, EIS and Polarization	Langmuir, Temkin and Freundlich isotherms	85.56%	49
34	Al (2.0M H_2SO_4)	Sweet almond oil	Seed oil	-	Mass loss, Hydrogen Evolution, PDP and EIS	Langmuir isotherm	93.62%	50
35	Al (3 Wt% NaCl)	*Ocimum basilicium*	Seeds	-	Weight loss, PDP, EDX, EIS, FTIR, SEM and EDS	Langmuir adsorption isotherm	95.5%	51
36	Al (1.0M HCl)	*Ziziphus spina christi*	Leaves	-	Mass loss, EIS, SEM, Polarization and ATR Spectra	Langmuir isotherm and Temkin adsorption isotherm	76.92%	52
37	Al (10% H_2SO_4)	Tulsi and Green tea	Leaves	-	Weight loss, FTIR, SEM, EDS, Polarization and XRD	-	71.43% and 85.71%	53
38	Al (1.0M HCl)	*Cichorium intybus*	Seeds	-	AFM, SEM, EDX, FTIR, UV Spectroscopy, Fluorescence and Contact angle measurement	Langmuir isotherm and DFT	93.67% Mixed-type inhibitor	54
39	Al (2.0N HCl)	*Solanum xanthoca-rpum* and *Salvodera persica*	Leaves and Stems	-	Weight loss and Gasometric analysis	-	94.00% and 92.63%	55
40	Al (0.01M HCl)	Milk thistle	Leaves	-	Weight loss and FTIR	Langmuir isotherm	86.00%	56
41	Al (0.4M H_2SO_4)	Coconut rice and eggshell	Seeds and Shells	-	Weight loss, SEM, EDX and XRF	-	73.50%	57

42	Al (1.0M HCl)	Sunflower (*Helianthus annuus*)	Stalks	-	Weight loss	Langmuir isotherm	93.30%	58
43	Al (0.5M HCl)	*Azadirachta indica* (Neem)	Seeds	-	PDP and FTIR	-	88.68% Mixed type of inhibitor	59
44	Al (0.01M NaOH)	Milk Thistle	Leaves	-	FTIR and Tafel Polarization	Langmuir isotherms	93.70% Mixed type of inhibitor	60
45	Al (0.1% NaCl)	Guar Gum	Gum	NaK $C_4H_4O_6 \cdot 4H_2O$	EIS, SEM, EDX and Tafel Polarization	-	90.00%	61
46	99.98% Al (1M HCl)	*Commiphora myrrha*	Gum	-	Weight Loss, EIS, FTIR, Polarization and SEM	Langmuir Isotherm, Fukui functions and Monte carlo simulation	89.90%	62
47	Al (1M KOH)	Grape leaf	Leaves	-	Weight loss and FTIR	-	87.44%	63
48	Al (3.5% NaCl-0.0125M H_2SO_4)	Maize husk	Husk (Shell of seeds)	-	Weight loss, PDP, OCP, OMC, XRD and XRF	-	-	64
49	Al (1.0M H_2SO_4)	*Hemero-callis fulva*	Plant	-	Weight loss, Temperature effect, PDP, OCP, EIS, SEM, EDX, AFM and XPS	Langmuir isotherm	89.00 % Mixed type of inhibitor	65
50	Al (HCl)	*Cuminum cyminum* (Jeeru)	Seed	-	Weight loss, Polarization, EIS and SEM techniques	-	88.39 % Mixed type of inhibitor	66
51	Al (HCl)	*Foeniculum vulgare mill* (Fennel)	Seed	-	Weight loss, Kinetic study, temperature effect	Langmuir isotherm	92.01 %	67
52	Al (1.0M HCl)	Pumpkin	Peel	-	Weight loss, AFM-XPS, EIS and PDP	Langmuir isotherm	95.42% Mixed-type inhibitor	68
53	Al (1.0M HCl)	*Ricinus communis* (Castor)	Seed	-	Gravimetric analysis and Thermodynamic study	Langmuir, Frumkin, Temkim and Flory-Huggins isotherms	83.93%	69

54	Al-AA3003 (1.0M HCl)	*Sapium ellipticum*	Leaf	-	Weight loss, EIS, FT-IR and RSM method	Langmuir isotherm	96.73% Mixed type of inhibitor	70
55	Al (0.75M HCl)	*Rosa* (Rose)	Flower	-	Weight loss, Kinetic study, Temperature effect and OCP	Langmuir isotherm	95.60 %	71
56	Al-AA2024-T3 (0.01M NaOH)	*Helianthus tuberosus L.* and *Poria cocos*	Root	Na_2SiO_3	Weight loss, AFM, XPS, FT-IR, EIS and PDP	Quantum chemical	98%	72
57	Al (20% cane ethanol and 80% gasoline blend solution)	*Annona muricata*	Leaves	-	Gravimetric, EIS, LPR, EN, SEM, FT-IR and GC-MS	Langmuir isotherm	90%	73
58	Al (0.5 M HCl)	*Musa paradisiaca*	Stem and sap	-	Weight loss, EIS, AFM and GC-MS	Langmuir, Temkin, Frumkin and Freundlich isotherms	90.73%	74
59	Al (2.0 M HCl)	*Moringa oleifera*	Leaves	-	Weight loss, AFM, PDP, EIS, FT-IR and PDP	-	90.10% Mixed type inhibitor	75
60	Al (0.5M HCl)	*Lagenaria breviflora* (Christmas melon)	Leaf	-	Weight loss, FT-IR and SEM	-	68%	76
61	Al (1.0M HCl)	Sweet Orange	Peel	-	Mass loss, EFM, PDP, EIS, EDX, SEM and AFM	Langmuir isotherm	92.53%	77
62	Al (1.0M HCl)	Yellow oleander	Flower	-	Mass loss, EFM, EIS, PDP, SEM, EDX and AFM	Langmuir isotherm	88.7%	78
63	Al (1.0M HCl)	*Xanthium spinosum*	Fruit	-	Gravimetric, PDP, EIS, EFM and AFM	Langmuir isotherm	93.1% Mixed type inhibitor	79
64	Al (0.1 and 1.0M HCl)	*Hibiscussabd ariffa*	Leaf	-	Weight loss, PDP, SEM and UV Spectroscopy	Langmuir isotherm	95.1 % and 96.2 % Mixed-type inhibitor	80
65	Al (0.2M HCl)	Red Onion	Peel	-	Weight loss and FT-IR	Langmuir and Freundlich isotherm	80%	81

| 66 | Al-1050 alloy (2.0M HNO_3) | Pomegranate | Peel | | Weight loss, SEM, FT-IR, UV-IR Spectroscopy, EIS, PDP, SEM, AFM, XRD and GC-MS | Langmuir isotherm, Quantum chemical | 92.58% mixed-type inhibitor | 82 |

3. Inhibition mechanism and characterization

Green inhibitors often lead to the formation of a stable, adherent and insoluble film on the aluminium surface. This film acts as a barrier, preventing aggressive corrosive agents such as oxygen, water and chlorides from reaching the metal surface[83]. The initial stage, an adsorption of inhibitor molecule represents in the development of a corrosion protective film or coating when exposed to aggressive media, occurring on the active sites of metallic surfaces[84]. Numerous factors influence the adsorption of inhibitors onto these surfaces, including the mode of adsorption, the chemical and electrochemical properties of the inhibitor, temperature, type of electrolyte used, steric effects, as well as the nature and surface charge of the metals[85]. The effectiveness of green inhibitors relies on the structure of their active components; numerous researchers have proposed various theories to elucidate how they work[86]. Green inhibitors, often derived from natural sources like plant extracts contain active compounds such as polyphenols, flavonoids, alkaloids and tannin. These molecules have functional groups such as $-OCH_3$, $-OH$, $-NMe_2$, $-NH_2$, $-NO_2$, $-CN$ and $-COOH$ that can interact with the aluminium surface[87, 88]. The FTIR spectra revealed the presence of phenolic hydroxyl (OH) and carbonyl (CO) groups in the *Acacia nilotica* powder. The spectra obtained from the inhibited metal surface showed shifts in the frequencies of these hydroxyl and carbonyl groups. FTIR analysis revealed various functional groups in the bioactive compounds of plant extract, such as O-H stretching, C=O stretching, C=C stretching, C-H bending and C-O stretching. It suggest that the active phytochemical constituents in the inhibitor interact with and bind to the metal surface[18]. Gas or liquid chromatography and mass spectrometry detect any volatile byproducts from the reaction or any breakdown products from the inhibitor. The inhibition process to occur through either physisorption or chemisorption[89,90]. Steady state adsorption which can involve either physisorption, chemisorption or a combination of both regarded as an ideal mechanism for effective corrosion inhibition[91]. Physisorption involves a weak polar interaction between the charged metal surface and inhibitor molecules, while chemisorption involves the molecules being strongly attached to the metal surface via robust electrostatic forces[92]. The surface morphology of the corroded samples both with and without *Ilex paraguariensis*, the aluminium immersed in 0.1 M HCl without an inhibitor experienced more corrosion compared to the sample exposed to degradation in the presence of the *Ilex paraguariensis* inhibitor[24].

The combined insights from adsorption isotherms study suggest that metal corrosion inhibition involves complex adsorption phenomena, often combining both physical and chemical interactions[93]. The adsorption can be monolayer or multilayer, influenced by lateral interactions, molecular size and surface coverage[94]. Effective inhibitors tend to form stable, possibly multilayered protective films through mechanisms that include both physisorption and chemisorption with their efficiency affected by intermolecular interactions and molecular size[95]. Potentiodynamic polarization analysis study the electrochemical corrosion current density, corrosion potential and the cathodic and Tafel anode constants were obtained from the curves[23]. Electrochemical studies, the presence of inhibitors shifts corrosion potentials and increases charge transfer resistance confirming that inhibition primarily occurs through adsorption and barrier formation, suggest to decrease corrosion rate[96]. These analysis show a change in surface composition, indicating reduced formation of corrosion products and the presence of inhibitor-derived species that stabilize the surface[97]. Spectroscopic analysis indicate that inhibition of inhibitor molecules contain functional groups capable of adsorbing onto the metal surface[98].

A theoretical study, Quantum chemical analysis like adsorption energy frontier molecular orbital energies (HOMO- LUMO gap) and charge distribution were correlated with experimental inhibition efficiencies, aiding in the design of more effectiveness of inhibitor[99]. The HOMO and LUMO orbitals, Fukui functions for nucleophilic (f^+) and electrophilic (f^-) attacks and electron density for indole molecule[33]. The electron density indicates a charge distribution

encompassing the entire molecule, suggesting that flat-lying adsorption orientations were most favorable. Molecular dynamic simulation study of adsorption and geometry of the verbascoside molecule on the Al(111) surface found the highest energy adsorption sites[37]. It indicate that interaction between aluminium surface and inhibitor molecules to created protective layer on metal surface. Certain inhibitors can modify the local pH near the surface, promoting the formation of a passive oxide layer[100]. A computational study analyzed corrosion inhibitor molecules of *Aegle marmelos* leaves extract[101], Parsley extract[102], *Ipomoea carnea* extract[103] and lemon leaf extract[104] as an aluminium using dual-modeling for aluminium. DFT calculations identified active sites and electron donation potential in bioactive molecules, while MD simulations confirmed the formation of a stable, hydrophobic protective film aligned with the Langmuir adsorption model. Some green inhibitors form complexes with aluminium ions or surface oxides. These complexes can stabilize the surface and inhibit further corrosion processes[105]. The investigation of individual phytochemicals and their constituents, the study of synergistic effects, the application of leaf extracts and the utilization of computational methods should be further explored in the area of plant-based corrosion inhibition for metals.

4. CONCLUSION

This review paper highlight the predominant research works carried out in recently investigated on the anti-corrosive property of eco-friendly and bio degradable inhibitor for aluminium metal and its alloy in present of corrosive medium. As per result of physiochemical methods, electrochemical methods and computational methods, the inhibition efficiency showed a positive correlation with increasing concentrations of the inhibitor. It shows the development trend will be more toward to preparation of non-toxic inhibitor for prevention of metal corrosion. It has been found that green inhibitor show inhibition efficiency up to 99.46%, indicate that plant extracts are highly effective corrosion inhibitors at different temperature. Some green inhibitors acts as a mixed-type corrosion inhibitor, affecting both the anodic and cathodic reactions. Computational study offers a comprehensive understanding of corrosion mechanisms at the atomic scale, enabling the development of more durable materials and protective strategies. Advancing green corrosion inhibitors support worldwide toward sustainable development and environmental preservation, making them a viable and eco- conscious choice for protecting aluminium structures and components.

ETHICAL APPROVAL: This review was conducted according to established guidelines for systematic reviews and meta-analyses. All sources were properly cited and the search strategy was transparently reported.

INFORMED CONSENT: The authors declare that there is no conflict of interest.

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