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#### Mini review

### An overview of sustainable green inhibitors for aluminum in acid media

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**Abstract:** Metal corrosion is a significant and growing area of study in industrial problems, which has found productive research ground in the field of green chemistry. In the last 10 years, green chemistry has been highlighting the importance of safeguarding human as well as the environmental well-being, in an economically advantageous way aiming at keeping away from reducing waste hazardous toxins, and pollutants. The era of metal degradation, commonly faced due to the usage of hazardous chemicals became very relevant and useful in the research area of chemistry. Even though several experiments have been conducted and, several research articles were published on this topic of nature-friendly green and clean inhibitors still there are yet a lot of things to be explored in this field for sustainable eco-friendly existence of human and natural interconnected existence. The main aim of the study is to provide a summary and describe the past authentic research that accounted in the research literature to employ eco-friendly corrosion inhibitors, especially extraction from leaves, stems, seeds, and fruits of the plants for aluminum alloy in acid solutions in the past decade. Weight loss and electrochemical approaches are among the most often utilized methods to measure corrosion rate and to evaluate the effectiveness of green corrosion inhibitors. The relevance of the area prompted the further study, leading to a large number of substances being evaluated.

Keywords: green inhibitor; aluminum; acid; adsorption; green solvent

**Abbreviations:** AFM: Atomic force microscopy; EDS: Energy dispersive spectrometry; EFM: Electrochemical frequency modulation; EIS: Electrochemical impedance spectroscopy; SEM: Scanning electron microscope; PDP: Potentiodynamic polarization; SES: Scanning electron study; WL: Weight loss; CR: Corrosion rate; h: Hour; DW: Distilled water

#### 1. Introduction

In 2012, Member States resolved to initiate a process to establish a set of SDGs (Sustainable Development Goals) based on the Millennium Development Goals and address the post-2015 development agenda at the UN Conference on Sustainable Development, often identified as Rio 20. By 2030, the SDGs seek to make a wealthier, equitable, and secure world. The 2030 Docket for Sustainable Development has 169 goals and 17 SDGs. These goals are the consequence of a new consultation mechanism that brought together national administrations and millions of people from across the world to explore and agree on a 15-year global path to sustainable development. These 17 goals are to be achieved by 2030. Thing 15.2 underlines the significance of biodiversity in a sustainable future. The part of biodiversity and ecosystem services has to be conceded in social, economic, financial, and environmental programs, along with their centrality to agriculture, fisheries, forestry, tourism, energy and mining, structure, manufacturing, and processing, and health diligence. This knowledge will be basic to achieving the goal. Human conditioning has led the resources to deplete. The agenda of sustainable development is on topmost precedence in the whole world. The utilization of natural resources must be cut back to achieve sustainable development. These social, economic, and environmental objects must be fulfilled. We cannot sustain development if we fall suddenly to maintaining an equilibrium of social, economic, and environmental objects. Natural resources must be guarded despite severe human activity then the role of educating and education for sustainable development is pivotal. Operation of resources was essential in the people around the world as we Indians find its evidence in our ancient literature like the Vedas. Sustainable development and environmental management depend on individual acts. The Vedic wisdom of India says that the terrain must be sustained and guarded. The exploitation of natural coffers degrades the environment. The consequences will be poverty and hunger, pollution, resource reduction, and a drop in the weal of the population. To safeguard the earth and our actuality we must adopt ways of co-existence in harmony with nature.

The continued processing of fossil-based feedstocks in the creation of chemical products including fuels and volatile organic solvents has aroused severe concerns about air quality degradation, safety, and health risks. As a result, various attempts are being undertaken to decrease the use of harmful compounds in chemical processes, as well as to reduce or eliminate waste. In both industry and academics, switching from commonly used fossil-based solvents to greener ones generated from renewable resources is a significant approach for achieving sustainability and safer and clean chemical processes.

It has become increasingly important in recent years to consider the long-term interests of present and future generations while pursuing sustainable development. Human-ecosystem equilibrium as a target aim of sustainability has been proposed, and sustainable development as an integrated strategy and a series of time-based processes that take us to that goal [1]. Environmental sustainability is closely related to green Chemistry. This term was first used in 1990 by the US Environmental Protection Agency (EPA) to encourage novel chemical technologies, and decrease or eradicate the utilization or creation of unsafe chemicals in the design, synthesis, and use of chemical goods. Basic scientific methodologies, such as those found in solvents, catalysis, synthetic methodology, analytical development, and the creation of safer chemicals with a raised awareness of their environmental effect are all included in the green chemistry movement's approach to protecting human health and the environment. Green chemistry and sustainability are based on the use of renewable raw materials in various industrial applications, according to this perspective. There has been an increase in interest in renewable raw materials as a result of nature's wide variety of chemical compositions.

Consequently, their interactions with their external conditions, corrosion is a normal occurrence in which alloys as well as metals effort to return to a more stable "thermodynamic state". Corrosion is costly owing to the loss of materials or their qualities, which results in lost time during maintenance, structural collapse, and shutdowns, which may be hazardous and cause damage in certain conditions [2]. The issue of corrosion is becoming more important as metals and alloys are used more often in contemporary life. One of the most significant non-ferrous metals, aluminum is used extensively in the food and packaging industry. Aluminum is a great conductor of electricity because of its excellent properties. Aluminum has mostly replaced copper because of this characteristic and several other inherent properties. This implies that aluminum is a thermodynamically reactive metal, second only to magnesium among major engineering metals [3]. Aluminum and its alloys are extremely resistant to corrosion in a wide range of conditions. In aqueous solutions, aluminum is known to behave passively. Metal corrosion has been linked to processes including metal ion move to the oxide/metal interface, oxygen ion and metal ion transfer to the solution/oxide interface, transferring an electron from the metal to acceptor species in solution, migration of ion in the oxide film, and all of which are associated with the passivating surface oxide film [4].

Typically, hydrochloric acid solutions are employed for pickling aluminum alloys as well as electrochemical and chemical etching operations, which often result in significant dissolution. For the removal of unwanted and undesirable scales, acid solutions are mainly used. In the cleaning process in industries generally, sulfuric and hydrochloric acid solutions are employed. As a result, several efficient inhibitors are applied to regulate metal dissolving and acid absorption [5]. Inorganic or organic molecules that adsorb on the metallic surface and separate it from its external environment to block the process of oxidation-reduction may be used in the corrosion inhibition procedure [6].

In acid media, nitrogen-containing organic compound means amines, alkaloid, quinine, nicotine, strychnine, papaverine, oxygen-containing functional groups such as ketone, aldehyde, ester, acetylenic compounds, and sulfur-containing compounds are used as corrosion inhibitors. Several studies have discovered nitrogen inhibitors number for metal and alloy corrosion inhibition in acid media.

Those organic inhibitors that include nitrogen are very effective at preventing the formation of metal in acidic solutions [7-13]. Furthermore, a variety of heterocyclic synthetic compounds were identified as corrosion inhibitors, and investigation into these molecules is currently ongoing [14]. Although several synthetic compounds exhibited strong anticorrosive performance, there was widespread concern about their toxicity to humans as well as the environment during the compound's synthesis or usage [15,16]. Typically, the reported inhibitors utilized in industries are very poisonous and environmentally dangerous.

Green inhibitors are gaining popularity in the corrosion meadow these days because of their biodegradability, safety, renewability, as well as ecological compatibility. These include amino acids [17], alkaloids [18], polyphenols [19], and plant extracts [20], which are widely disseminated

and have minimal economic value, as well as byproducts of agro-industrial operations and agricultural waste. Chitosan oligomers are soluble over a wide pH range from acidic to basic ones. On the contrary chitosan derivatives with higher molecular weight are only soluble in acidic aqueous even at high deacetylation degrees. This is the favorable property for corrosion inhibition, and therefore, chitosan derivatives are nowadays used as corrosion inhibitors for metal dissolution [21–24]. Corrosion inhibitors that are safe for the environment may be found in natural materials because most of their extracts contain necessary elements like oxygen, nitrogen, carbon, and sulfur, which are active in organic molecules and aid in the adsorption of such molecules on alloys or metals to create a film that protects the exterior sides and prevents corrosion. N, S, and O-containing chemical substances are found in their barks, leaves, fruits, and seeds and some of them are efficient inhibitors of metal and alloy corrosion in a variety of severe settings. The quantity of adsorbed inhibitors on the metal surface determines the inhibition efficacy. As shown in Figure 1, the documentation on the subject of green corrosion inhibitors for metal surfaces is primarily active. Figure 1 shows the published research articles on the topic of green corrosion inhibition that were found using a SciFinder literature survey [25]. The increasing rate of publication indicates an exponential trend. As a result, the current review paper discusses the application of prospective green "eco-friendly inhibitors" on the surface of aluminum metal in acidic solutions as effective corrosion inhibitors.

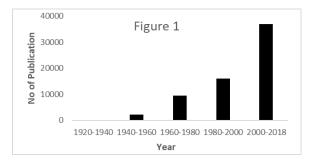


Figure 1. Year-wise publication.

#### 2. Experimental

A general description of the method used by research workers to determine corrosion rates is as follows.

#### 2.1. Weight loss

The traditional mass loss technique may be utilized to assess the corrosion rate. Using this approach, the mass loss of metal owing to exposure to corrosive fluids for a certain period and computing the variation in weight before and after immersion may be determined. For the immersion period, acid solution with and without inhibitors was used to immerse aluminum alloy/metal test specimens. Extraction from the plants was used as an inhibitor having appropriate concentration. The specimens were hanging with aid of a glass hook. After a certain period of exposure, specimens were taken out and washed with a cleaning solution by washing them twice with double distilled water, drying them, and then weighing it, corrosion products were removed. The mass loss was determined

by comparing the pre-and post-exposure weights of the specimens. The following formulae (1) to (3) were used to compute the rate of corrosion, surface coverage degree ( $\Theta$ ), and inhibition efficiencies: the corrosion loss in the uninhibited system is represented by  $W_u$ , while  $W_i$  is represented as corrosion loss is inhibited.

$$CR \ (mpy) = \frac{534W}{DAt},\tag{1}$$

$$\eta\% = \frac{Wu - Wi}{Wu} \quad x \quad 100, \tag{2}$$

$$\Theta = \left(\frac{Wu - Wi}{Wu}\right),\tag{3}$$

where D represents the density of metal specimen, W represents the metal mass loss in grams, metal sample surface area in inches square is represented by A and 't' represents a time for immersion in hours.

When electrochemical corrosion begins, the current flowing between the cathode & anode creates polarization, which is a change in the electrode potential.

#### 2.2. Potentiodynamic polarization

A sample is subjected to polarization procedures to alter its current or potential, which are then recorded. There are two ways to do this: either using AC (alternating current) or DC (direct current) [5]. The following are a few of the most widely used and essential approaches.

Tafel Extrapolation: anodic and cathodic processes in an electrochemical cell are shown by Tafel curves, a current potential diagram. Working electrode (metal sample) potentials are adjusted at a precise pace and the resultant current response is recorded in this approach. A total current is produced by the simultaneous anodic and cathodic reactions, which is signified by a curve line. The logarithmic Tafel plot's linear sections are inferred to create an intersection that offers a point of reference that represents the "corrosion rate" and inhibition efficacy calculations based on Eqs (4) and (5), respectively.

$$CR \ (mpy) = \frac{(0.13 \times i_{corr} \times E.W.)}{n \times d},\tag{4}$$

where the equivalent weight of the aluminum metal in grams is denoted by 'E.W.', corrosion current density ( $\mu A$ ) by 'i<sub>corr</sub>', electron number by 'n', metal density by 'd' and metric, and the time conversion factor are 0.13.

$$\eta(\%) = \left[\frac{i_{corr}(u) - i_{corr}(i)}{i_{corr}(u)}\right] \ x \ 100, \tag{5}$$

where corrosion current densities values with icorr(i) and without inhibitor icorr(u) were calculated using Eq (5), whereas ( $\eta$ %) percentage efficiency (percent) was derived from the graph.

## the $R_{ct}$ in the absence and presence of the inhibitor values is represented by $R_{ct}$ and $R_{ct(inh)}$ . correspondingly.

By using Eq (9) the IE percent (percentage inhibition efficiency) from the  $R_t$  values [34]:

 $\eta(\%) = \left[\frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}}\right] x 100,$ 

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# This approach is non-destructive [26], has rapid application, may be utilized in the field with portable equipment [27], and is the most employed electro-chemical method [28]. The LPR principle is to spread the corrosion equilibrium over the metal surface by using a modest perturbative DC electrical pulse. The equilibrium's reaction to this perturbation is assessed in comparison to a source half-cell [29]. At the free corroding potential, the polarization $\Delta E/\Delta i$ potential current density curve slope. The Stern-Greay approach, in which the cathodic and anodic Tafel slopes may be empirically determined from actual polarization plots, can be used to connect the LPR to the corrosion current.

The inhibitory efficiency has been derived from the observed polarization resistance value with the following formula:

$$\eta(\%) = \left[\frac{R'_p - R^0_p}{R'_p}\right] \ x \ 100, \tag{6}$$

where polarization resistance  $R_P^{'}$  and  $R_P^{0}^{'}$  are with and without inhibitor, correspondingly.

#### 2.4. EIS (Electrochemical impedance spectroscopy)

2.3. LPR (Linear polarization resistance)

This is a potent method that may be used to evaluate coatings in corrosion studies. Useful information is gained by using this method to determine the effectiveness of an inhibitor. An AC voltage (in potentiostatic EIS case) or current (in galvanostatic EIS case) is given to the system understudies to get a response in voltage (current) or current (voltage) form as a frequency function. Using potentiostat-galvenostat and a frequency response analyzer, this procedure may be conducted in a three-electrode setup (FRA) [30]. On the basis of the Nyquist plot shape, an AC voltage with minor perturbations of 5 mV to 10 mV is given in the system throughout a frequency range generally beginning from 100 kHz to 10 mHz, an equivalent circuit comprises information on  $R_s$  ("solution resistance"),  $C_{dl}$  ("double-layer capacitance"), and  $R_{ct}$  ("charge transfer resistance") to represent the electrochemical cell including the metal sample, electrolyte medium, as well as adsorbed inhibitors. As inhibitor concentrations increase, the  $R_{ct}$  value increases, whereas the  $C_{dl}$  value decreases [31].  $R_{ct}$  values have been evaluated by deducing the high from the low-frequency impedance, as shown below [32]:

$$R_{ct} = Z$$
 (at low frequency) – Z (at high frequency). (7)

The following equation was used to compute the values of Cdl at fmax frequency, where the imaginary impedance component is maximum ( $Z_{max}$ ) [33]:

$$C_{dl} = \left[\frac{1}{2\pi f_{max}}\right] \left[\frac{1}{R_{ct}}\right]. \tag{8}$$

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#### 2.5. Scanning electron microscope

It is a kind of microscope that utilizes a centered electron beam to produce pictures of a specimen. Several signals may be recorded that provide information regarding the specimen's surface geography and composition when electrons contact atoms in the sample. When scanning the electron beam using a raster pattern, the received signal and the beam's position are combined to generate an image. One nanometer resolution is possible using SEM. High vacuum, low vacuum, moist, and high-temperature specimens may all be inspected. Atoms energized by an electron beam emit secondary electrons, the most common kind of electron. This plume is mostly covered by a sample on a flat surface, however, on a tilted one the plume is partially revealed and most secondary electrons are released. When the specimen is examined and the "secondary electrons" are seen, a picture of the surface topography is created [35].

For SEM examination, aluminum samples were immersed in the acid solution for a predetermined period. A nitrogen stream was used to dry the samples after they were removed from the solutions and cleaned with deionized water. To further understand the surface's morphology, SEM was used.

#### 3. Discussion

Natural materials and plant extracts may be used as corrosion inhibitors, and this research aims to gather a bibliography of relevant studies. The necessity of emphasizing the weak spots and insufficiencies in the green inhibitors area as constructive criticism to re-analyze the literature and recognize future work in the subject that often lacks rationality is emphasized in particular. Table 1 contains a list of all the extracts that were used as green corrosion inhibitors and would be discussed in the study. There is a table in the published work of the previous ten years that describes their respective natural source, extraction solvent, protected metal& corrosive environment, the inhibition efficacies, and other relevant information.

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[36]	Tender arecanut	DW,	Al	0.5 M HCl	WL,	94.44	Langmuir
	seed (TAS)	Soxhlet 6 h			polarization,		
					EIS		
[37]	Dry arecanut seed	DW,	Al	0.5 M HCl	WL,	94.45	Langmuir
		Soxhlet 7 h			polarization,		
					probe method		
[38]	Trigonella foenum	DW, 24 h	Al 99.2%	1 M HCl	WL, 308–338	86.53	Langmuir
	graecum seed				K, PDP, EIS,		
	(Fenugreek)				HPLC		
[39]	Milk thistle leaves	DW,	Al AA7051	0.01 M HCl	WL, PDP	86.41	Langmuir
		Soxhlet 7 h					

Table 1.	. References	and result	s of research	done by	the author.

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
40]	Coriandrum sativum	DW	Al 99.61%	1 M H <sub>3</sub> PO <sub>4</sub>	EIS, PDP,	72.75	Langmuir
	leaves				SEM, 303-		
					333 K		
[41]	Irvingia gabonensis	DW, 24 h	Al	1 M HCl	WL,	97.36	Langmuir
	plant				temperature		
[42]	Cantaloupe juice &	DW	Al alloy	0.5–1.5 M	WL	92.75, 71.60	Langmuir,
	seed		32177	HCl			Temkin
[43]	Date palm leaves	DW, 3 h,	Al 98.8%	1 M HCl	WL, 293–323	87.8	Langmuir
		253 K			K, SEM, EDS		
[44]	Carcia papaya seeds	DW	Al 98.84%	2 M H <sub>2</sub> SO <sub>4</sub>	PDP, EIS,	96.70	Langmuir
					SEM		
[45]	Melia azedarach	DW, 6 h	Al 99.99%	2 M HCl	WL, PDP, EIS	86.2	Langmuir
-	leaves						-
[46]	Olive seeds	DW,24 h	Al 98.63%	1 M HCl	WL, 303–313	98.86	Langmuir
					K, EIS, SES		C
[47]	Tinosporacordiofolia	DW, 5 h,	Al	H <sub>2</sub> SO <sub>4</sub> (PH	PDP, 303–323	88.02	Langmuir
	stems		98.84%	= 3)	K, EIS, FT-IR		C
[48]	Calotropis gigantea	DW	Al 98.02%	0.4–0.6 M	WL, 313–333	84.31	Langmuir,
	leaves			HCl	K		Freundlich,
							Temkin
[49]	Cissus populnea	DW	Al 99.8%	0.5 M HCl	WL	72.63	Langmuir,
	stem						Freundlich,
							Temkin, Flory-
							Huggins
[50]	Bacopa monnieri	DW, 5 h	Al 99.54%	0.75-1.25	WL, PDP, EIS	91.85	Langmuir
	leaves	,		M HCl	, ,		5
[51]	Tulsi (Ocimum	DW, 1 h	Al 99.54%	0.75–1.25	WL, 313–333	85.17	Langmuir
	scantum) leaves	,		M HCl	K, PDP, EIS		0
[52]	Azadirachta indica	DW, 3 h	Al A-63400	0.5 M HCl	WL, 313–333	84.96	Langmuir,
	leaves	,		-	K		Freundlich
[53]	Cumin seeds	DW, 2 h	Al 99.54%	1 M HCl	WL, PDP,	88.39	Langmuir
		,		-	EIS, SEM		0
[54]	Calotropis gigantea	DW	Al 98.02%	0.4–0.6 M	WL,	84.31	Freundlich
	leaves			HCl	polarization		
[55]	Aloe Plant	DW	Al 95.2%	0.5 M HCl	PDP, EIS	80.01	Freundlich
[56]	Bitter Kola	DW	Al 98.76%	0.5 M HCl	WL, 303–333	82.96	-
L- ~]					К		
[57]	Sida acuta stem	DW	Al-Cu-Mg	0.5 M HCl	WL	93.63	_
L <sup>2</sup> ' ]	Sina actual stem	2.11	Alloy	5.5 111101		20.00	
			95.5%				

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[58]	Beet root	DW	Al 95%	H <sub>2</sub> SO <sub>4</sub> (PH	WL, influence	98.0	-
				= 3)	of Zn, PDP,		
					EIS, FT-IR,		
					fluorescence		
[59]	Yellow colour ripe	1% HCl,	Al A-63400	0.5 M HCl	WL, 303–323	83.33	Langmuir
	arecanut husk	Soxhlet 24 h			К,		
					polarization,		
					EIS		
[60]	Spondias mombin	0.5 M	Al	0.5 M	WL, 30–60 □,	80.3,	Langmuir
	leaves	H <sub>2</sub> SO <sub>4</sub> ,		$H_2SO_4$	KI	95.1(with KI)	
		reflux 3 h					
[61]	Murraya Koengii	HCl	Al	HCl	polarization,	91.79	Langmuir
	leaves (Curry)			medium of	EIS		
				pH 3			
				solution			
[62]	Newbouldia laeyis	HCl, 3 h	Al AA5052	0.5 M HCl	WL, 298–313	87.0	Langmuir,
	leaves				K, PDP, SEM		Temkin
[63]	Piper guineense	1 M HCl,	Al 98.47%	1 M HCl	WL, 303–353	95.34	Langmuir
	seed	reflux 3 h			Κ		
[64]	Carica papaya	1 M H2SO4,	Al 98.94%	1 M H <sub>2</sub> SO <sub>4</sub>	WL, 303–323	70.0	Langmuir
	leaves	24 h			K, SEM, FT-		
					IR		
[65]	Papaya peel fruit	1 M HCl,	Al alloy	1 M HCl	Polarization,	98.1	Langmuir
	(Carica Papaya)	reflux 5 h			EIS, SEM		
[66]	Aspilia africann	HCl, 3 h	Al AA3003	0.4 and 0.5	WL,	95.0	Langmuir,
	leaves			M HCl	polarization,		Temkin
					EIS		
[67]	Nipah palm (Nypa	2 M HCl	Al	2 M HCl	WL	51.43	Langmuir
	fruticans)		99.98%				
[68]	Cinodosculus	HCl, 3 h	Al 98.84%	1 M HCl	WL, additives	58.0	Langmuir
	chayamansa leaves	boil			KI		
[69]	Hibiscus sabdariffa	1 M H <sub>2</sub> SO <sub>4</sub> ,	Al Pure	0.5 M	WL, PDP,	94.0	Langmuir
		boiled for 3		$H_2SO_4$	EIS, 298–333		
		h			Κ		
[70]	Azadirachta indica	HCl, 2 h	Al 93.10%	1.85 M HCl	Gasometric	-	Langmuir,
	leaves				RT, SEM		Freundlich,
							Frumkin, Temkin
[71]	Terminalia ivorensis	0.5 M HCl,	Al AA8011	0.5 M HCl	WL	89.56	Temkin
		3 h					
[72]	Veronia amygdalina	HCl, 2 h	Al 99.0%	2 M HCl	Gasometric	99.9	Temkin

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[73]	Camellia sinensis (green tea)	0.5 M HCl	Al 99.0%	0.5 M HCl	WL	90.57	Freundlich
[74]	Orange seed	HCl, reflux 3 h	Al	1 M HCl	WL	38.37	-
[75]	Azadirachta indica	HCl	Al 99.54%	0.75–1.25 M HCl	WL, PDP, EIS, SEM	96.41	-
[76]	Azwain seed	-	Al	0.5 M HCl	WL, polarization, EIS, SEM	90.0	Langmuir, Frumkin
[77]	Andrographis paniculate plant	-	Al 98.8%	HCl medium of pH = 3 solution	Polarization, EIS, 303–323 K, SEM	91.7	Langmuir
[78]	Ajowan plant	-	Al	0.5 M HCl	WL, polarization, EIS	80.98	Langmuir
[79]	Capparis decidua	-	Al 99.99%	1 M HCl	WL, polarization, EIS, SEM	88.2	Langmuir, Temkin
[80]	Jasminum nudiflorum lindl leaves	-	Al	1 M HCl	WL, polarization, EIS, SEM	-	Langmuir
[81]	Dendrocalamus brandisii leaves	-	Al	0.5–3 M HCl & H3PO4	WL, polarization, EIS, SEM	91.30, 47.1	Langmuir
[82]	Morinda tinctoria leaves	-	Al	0.5 M HCl	WL, additives KCl, KBr, KI	-	Langmuir
[83]	Thymus algeriensis roots & leaves	-	Al 2024	1 M HCl	WL, 298–338 K, gasometric, EIS	78.7	Langmuir
[84]	Coriander seeds	-	Al 99.20%	1 M HCl	WL, PDP, EIS, GC-MS	82.49	Langmuir
[85]	Shatavari (Asparagus racemosus)	-	Al 99.60%	1 M HCl	WL, 288–303 K, SEM, quantum chemical analysis	80.54	Langmuir

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition efficiency (%)	Adsorption isotherms
[86]	Phoenix dactylifera leaves, male &	-	Al commercial	1 M HCl	WL, 313–333 K	88.70 male, 95.16 female	Langmuir, Freundlich,
	female						Frumkin,
							Temkin, El-
							Awady, Flory-
							Huggins
[87]	Cassia alata leaves	Alcohol, 48	Al	1 M HCl	WL, 303–353	87.67	Langmuir
		h			К,		
					FTIR, UV, EDX		
[88]	Azadirachta indica	Ethanol,	Al 98%	0.5 N HCl	WL, 303–353	92.37	Langmuir
	fruit	Soxhlet, 24 h			K, FTIR		
[89]	Tussilago farfara	Methanol	Al 99.98%	2 M HCl	Gassomatry,	94.2	Langmuir
		(70%), 48 h			WL, PDP,		
					EIS, EFM		
[90]	Juglans regia	Methanol	Al 99.98%	2 M HCl	Gassomatry,	98.7	Langmuir
		(70%), 48 h			WL, PDP,		
					EIS, EFM		
[91]	Trigonella foenum	Ethanol	Al AA6063	0.5 M HCl	WL, additives	83.3	-
	gracenums seed				$Zn^{+2} > Br^{-} >$		
					Cl > I		
[92]	Тесота	Non	Al	$1 \text{ M} \text{H}_2 \text{SO}_4$	WL, PDP,	90.20	Langmuir
		aqueous			EIS, EFM		
		solvent					
[93]	Bassia muricata	Ethanol	Al 99.55%	1 M	WL, 298–318	90.0	Temkin
		4 days		H2SO4	K, PDP, EIS, EFMc		
[94]	Ficus carcia leaves	Methanol	Al alloy	0.5 M HCl	WL, 303–333	91.34	Langmuir,
					Κ		Frumkin
[95]	Ziziphus mauritiana	Ethanol,	Al	0.5 M HCl	WL	76.80	Langmuir
	fruit	Soxhlet 24 h					
[96]	Green coffee bean	Methanol	Al	Acid rain	PDP, 303–333	98.08	Langmuir
		(99.8%), 48			Κ		
		h					
[97]	Breadfruit peels	Acetone	Al	0.5 M	WL, 303–333	85.3	Langmuir
		(50%)		H2SO4	К		
[98]	Ziziphus jujube	Methanol	Al 95.9%	1 M HCl	WL, SEM	91.26	Langmuir
	leaves	(80%), 5 h					

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[99]	Black mulberry	Ethanol, 6 h	Al 99.99%	2 M HCl	WL, PDP,	93.44%	Langmuir
	fruits (Morus nigra)				hydrogen evolution	98%	
[100]	Veronia amygdalina	Ethanol,	Al	1 M HCl	WL, 303–333	99.10%,	Langmuir,
	leaves	DW, HCl			K	94.3%, 92.0%	Flory Huggins
[101]	Ocimum	DW,	Al AA1066	1 M HCl	WL	DW>	Langmuir,
	gratissimum leaves	ethanol, 1 M HCl				ethanol > 1 M HCl	Flory Huggins
[102]	Withania somnifer	Ethanol,	Al	0.5, 1, and	WL, 303–333	98.53	Langmuir
	leaves & root	Soxhlet	commercial	2 M HCl	Κ		
[103]	Basil	Ethanol,	Al	0.5–3 M	WL	97.09	Langmuir
		Soxhlet	98.5%	HC1			
[104]	Coconut coir dust	Acetone, 48 h	Al 98.60%	1 M HCl	WL, hydrogen evolution,	80.0	Langmuir
					FTIR, 303– 333 K		
[105]	Cumin seeds	Methanol,	Al	1 M HCl	WL, 308–338	99.6	Langmuir
		24 h			Κ,		
					polarization, EIS		
[106]	Albizia lebbeck seed	Alcohol, 48 h	Al	1 M HCl	FTIR, WL, 303–333 K	92.31	Langmuir
[107]	Portulaca oleracea	Ethanol, 48	Al	2 M H <sub>2</sub> SO <sub>4</sub>	WL, 305–315	45.16	Langmuir,
	leaves	h	commercial		K		Freundlich, Temkin
[108]	Manihot esculentum	Ethanol, 48	Al	2 M H <sub>2</sub> SO <sub>4</sub>	WL, 305–315	50.0	Freundlich, El-
	leaves	h	commercial		К		Awady
[109]	Manihot esculentum	Ethanol, 48	Al	2 M H <sub>2</sub> SO <sub>4</sub>	WL, 305–315	43.33	Langmuir,
	root peel	h	commercial		К		Freundlich, Temkin
[110]	Phoenix dactylifera	Petrolium,	Al 99.55%	0.5 M HCl	PDP, EIS,	89.1 & 91.8	Langmuir
	plant	ether and	& 92.48%		EFM, 293–		
		methanol			333 K		
[111]	Garlic (allium) skin	Acetone	Al 97.58%	0.5 M HCl	WL, 303–323	95.0	Langmuir,
					Κ		Temkin
[112]	Murraya Koenigii	Ethanol	Al alloy	0.5 M HCl	WL, 303–333	96.43	Langmuir
	leaves		6063		K		

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[113]	Sorghum bicolor	Ethanol, 48	Al 99.8%	2 M H <sub>2</sub> SO <sub>4</sub>	WL, 305–315	50.0	Langmuir,
	leaves	h			K		Freundlich,
							Temkin, El-
							Awady
[114]	Sapium ellipticum	Ethanol, 48	Al 97.0%	1–2 M HCl	WL, 303–333	96.73	Langmuir
	leaves	h			K, PDP, SEM		
[115]	Azadirachta indica	Ethanol, 7	Al 98.50%	0.5–2 M	WL, 303–333	54.60	Langmuir
	leaves	days		HCl	Κ		
[116]	Kola nitida seeds	Ethanol, 48	Al AA3003	0.1 M HCl	WL, PDP, EIS	85.0	Langmuir
		h					
[117]	Nicotiana tabacum	Ethanol, 48	Al AA3003	0.1 M HCl	WL, PDP,	84.80	Langmuir
	leaves	h			EIS, EFM,		
					SEM		
[118]	pawpaw (Carica	Ethanol, 48	Al 99.50%	1 M HCl	WL, 303–333	81.99	Langmuir,
	papaya) leaves	leaves h K, PDP, FT-IR		Frumkin,			
							Temkin, Flory-
							Huggins
[119]	Jatropha curcas	Ethanol	Al	1 M HCl	WL, 303–333	76.49	Freundlich,
	leaves	(96%), 72 h	AA60		K		Temkin, El-
							Awady,
[120]	Dry arecanut seed	Hexane, 5 h	Al A-63400	0.5 M HCl	WL, 303–323	83.33	Langmuir
					K, PDP, EIS,		
					SEM, AFM		
[121]	Peganum harmala	Methanol,	Al Alloy	1 M HCl	WL, 298–313	89.0	Langmuir
	plant	2 h	6063		K, PDP		
[122]	Persea Americana	Ethanol	Al	1 M H <sub>2</sub> SO <sub>4</sub>	WL, 313–333	78.90	Langmuir,
	leaves (Avocado	48 h			Κ		Temkin
	pear)						
[123]	Phyllanthus amarus	Ethanol	Al	1 M HCl	WL, 303–333	93.93	Langmuir,
	leaves	48 h			K, PDP,		Freundlich
					quantum		
					chemical		
					study, SEM		
[124]	Acacia senegalensis	Ethanol,	Al	0.5 M	WL, 313–343	92.66	Langmuir
	stem	48 h		$H_2SO_4$	K, PDP, SEM		
[125]	Cordia dichomota	Ethanol	Al AA6063	0.5 M HCl	WL, 293–353	90.63	Langmuir, El-
	seeds	24 h			K, PDP, EIS,		Awady
					SEM, FTIR		

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[126]	Hemerocallis fulva	-	Al	1 M H <sub>2</sub> SO <sub>4</sub>	WL, 303–333	89.0	Langmuir
					K, PDP, EIS,		
					AFM, SEM,		
					FTIR		
[127]	Euphorbia neriifolia	Ethanol,	Al	1–3 M	WL,	92.62	Langmuir
	linn	15–20 h	commercial	HNO <sub>3</sub>	thermometric		
[128]	Euphorbia neriifolia	Ethanol,	Al	1–3 M HCl	WL,	94.92	Langmuir
	linn	15–20 h	commercial		thermometric		
[129]	Fennel seeds (F.	Methanol	Al 99.54%	0.75-1.25	WL, 313–333	92.01	Langmuir
	Vulgare)			M HCl	Κ		
[130]	Strichnos spinosa	Ethanol	Al 98.70%	0.3 M HCl	WL, 303–323	88.48	Langmuir,
	leaves	(95%), 2			K, PDP, SEM,		Freundlich
		days			Ft-IR		
[131]	Capparis decidua	Ethanol, 48	Al 98.02%	1–3 M HCl,	WL, 303–323	98.73, 94.02,	Langmuir
	fruits, stem & roots	h		0.5–2 M	K	94.92 for HCl	
				$H_2SO_4$		and	
						62.92,69.54	
						80.22, for	
						$H_2SO_4$	
[132]	Treculia African	Ethanol, 3	Al AA1066	1 M HCl	WL, 303–333	74.17	Freundlich,
	leaves	days RT			K		El-Awady
[133]	Dryopteris cochleate	Methanol, 3	Al 98.5%	1 M H <sub>2</sub> SO <sub>4</sub>	WL, 298–338	84.62	Freundlich
	leaves	h			K, PDP, EIS,		
					SEM, FT-IR		
[134]	Allamanda	Methanol,	Al AA8011	1 M HCl	WL, 303–323	85.0	Freundlich
	cathartica leaves	24 h			K		
[135]	Chrysophyllum	Ethanol	Al 99.0%	1.5 M	WL, 303–333	40.52	Temkin
	albidum fruit	95%		H <sub>2</sub> SO <sub>4</sub>	К		
[136]	Prosopis laevigata	Methanol,	Al	0.5 M	WL, 293–333	93.53	Frumkin, Temkin,
	leaves	24 h		H <sub>2</sub> SO <sub>4</sub>	K, PDP, EIS		
[127]	T	Alcohol, 48	A 1	0.5 M HCl	WI 202 222	94.50	Temkin
[137]	Lawsonia inermis		Al	0.5 M HCI	WL, 303–333	84.52	Temkin
	seed	h			K, EDAX,		
[120]	Anogoiagua	Etheral 1	A 1	020014	FTIR, UV	05.19	
[138]	Anogeissus	Ethanol, 1	Al	0.2–0.8 M	WL, 308–338	95.18 $I > Pr > C1$	-
	leiocarpus leaves	week	98.70%	HCl	K, addatives	I > Br > Cl	
[120]	Congregation	Ethonal	A1 00 000/	05.2 M	KCl, KBr, KI	74.14	
[139]	Gongronema	Ethanol	Al 98.98%	0.5–2 M	WL, 303–333	74.14	-
	latifolium			HCl	K		

Ref.	Inhibitors	Extract	Metal	Solutions	Methods	Inhibition	Adsorption
						efficiency (%)	isotherms
[140]	Polygonatumoda	Methanol,	Al 99.89%	1 M HCl	WL, 303–333	94.70	-
	ratum leaves	24 h			K, PDP, EDX,		
					SEM		
[141]	Talinum triangular	Ethanol, 48	Al Alloy	1–1.5 M	WL, 303–333	62.30 & 63.27	-
	leaves & Musa	h	ZA-27	HCl	K		
	sapientum peel						
[142]	Garlic	Ethanol	Al	0.05 M	WL, 303–333	90.0	-
				H <sub>3</sub> PO <sub>4</sub>	K, PDP, EIS,		
[143]	Solanum	Ethanol	Al	2 M HCl	WL,	83.85 stem,	-
	xanthocarpum stem		commercial		gasometric	94.53 leaves	
	& leaves						
[144]	Acanthocereus	Aqueous	Al	1 M HCl	EIS,	7.5	-
	tetragonus				polarization		

The category of extraction solvent and the separation process could have an important influence on the yield of materials extracted from plant materials. Each extraction method has distinct operating parameters that influence the content and antioxidant action of the extract and is essential to be optimized. The solvent to temperature, feed ratio, extraction time, number of repetitive sample extractions, and the ideal of extraction solvents are primary factors monitoring extraction reactions. Solubility is extremely impacted by the temperature and extraction time. At the greater extraction rate, surface tension, viscosity, and temperature of solvents decrease, which motivates rates of the mass transfer [145]. Material pretreatment, which influences the particle size, distribution, sample matrix, and moisture content is another factor that influences the extraction rate [146].

The majority of the utilized solvents were documented as being of environmental worry. These worries arise in 3 parts: (1) the solvent's source and production; (2) its properties in usage, counting accidental discharge; (3) and disposal. There is widespread agreement among proponents of solvent usage in the literature that a solvent or group of solvents must be considered characteristically green. Solvents and their groups that were recommended as green solvents included water, ionic liquids, supercritical fluids, gas extended liquids, and solvents derived from biomass [147]. Biomass is an exceptional renewable substitute resource for manufacturing bio-solvent alcohol. Most of the researchers used methanol and ethanol as a solvent for the extraction while some used the acid solution itself as a solvent, and used as a corrosion inhibitor and noted extraordinary inhibition efficiency, which can be shown in column III of Table 1. Because alcohol is well recognized to be safer for human use and it is widely used for the "anthocyanin-rich phenolic" compounds extraction and also applied to obtain flavonoids from plant tissues.

Adsorption is the 1<sup>st</sup> stage of developing a corrosion-protective coat or film on a metallic surface in active locations in the existence of aggressive media. Many variables influence the inhibitor adsorption on the "metallic surface" and its isolation such as adsorption mode, electronic and chemical features of the inhibitor, kind of electrolyte applied, temperature, steric effect, and the type and surface charge of the metals [148]. An adsorption isotherm is a useful tool for explaining the corrosion inhibition process. Adsorption on metal surfaces is frequently categorized as physisorptions or chemisorptions, based on the interaction strength between the surface as well as the absorbed molecule. The connection between inhibition effectiveness and the majority of inhibitor content at a constant temperature, recognized as isotherm [149], gives information about the adsorption process.

The metal corrosion inhibition by extract were accredited to their adsorption on to aluminum metal alloy surface. This may be generally established from the experimental data fitness to several adsorption isotherms but most fitted is as Langmuir [36–53,59–70,76–131]. Temkin [42,48,62,66,70–72,79,86,93,107,109,111,113,118,119,122,135–137], Frumkin [76,86,94,118,136], Freundlich [48,52,54–55,70,73,86,107–109,113,119,123,130,132–134], Florry Hugginsn [49,86,100–101,118] and El-Awardy [86,108,113,119,125,132] isotherms are frequently used by the researcher. The general form of above all isotherms is presented as below [150]:

$$f(\theta, x) \exp(-2\alpha\theta) = KC. \tag{10}$$

Here,  $f(\theta,x)$  denotes a configurationally factor,  $\theta$  indicates the surface coverage area, x represents the size ratio, K represents the equilibrium constant,  $\alpha$  denotes the parameter of molecular interaction, and C signifies the inhibitor concentration, based on the physical paradigm and assumptions behind the isotherm derivative [151].

Table 1 of column VIII displays the assessments of "Langmuir isotherm" with other models like Frumkin, Temkin, Freundlich, Florry Hugginsn, and El-Award. Langmuir isotherm typical adopt that the process of the adsorption happens on definite homogeneous sites on the metal surface and it is utilized to countless outcomes in numerous monolayer adsorption processes [152]. The following equation was applied to compute the Gibbs free energy of adsorption ( $\Delta G^0_{ads}$ ).

$$\log {P_1}/{P_2} = {E_a}/{2.303RT} \left[ {1}/{T_1} - {1}/{T_2} \right], \tag{11}$$

where C is the inhibitor concentration and  $Log B = -1.74 - \frac{\Delta G_{ads}^0}{2.303RT}$ . The  $\Delta G_{ads}^0$  values of all tested green inhibitors were found to be negative and evidence that the inhibitor concentration rises the  $\Delta G_{ads}^0$  values decrease in order, showing that the most effective inhibitor displays more negative  $\Delta G_{ads}^0$  value. This indicates that they are well adsorbed on the metal surface. Usually, the  $\Delta G_{ads}^0$  values are less negative as compared to  $-20 \text{ kJ} \cdot \text{mol}^{-1}$  represents physical adsorption whereas those are more negative as compared to  $-40 \text{ kJ} \cdot \text{mol}^{-1}$  signifies chemical adsorption [153,154]. In most of the tested green inhibitors attached adsorption the inhibition effectiveness with temperature rise specifies physical adsorption.

The following Arrhenius Equation was applied to compute the Ea ("Activation Energy") (12). Here  $P_1$  and  $P_2$  represent the corrosion rate at temperatures  $T_1$  and  $T_2$  respectively.

$$Log P_1/P_2 = \frac{E_a}{2.303RT} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right].$$
(12)

In all the tested green inhibitors, it is observed that acid comprising inhibitors' mean values of Ea are observed to be greater than the uninhibited system. The greater Ea values in the existence of inhibitors evaluated to the "blank coupled" with a drop in the inhibition effectiveness with temperature rise may be interpreted as assign of physical inhibitor adsorption on the metal surface [155]. Greater Ea values in the existence of extract may also be connected with the rise in double-layer thickness that improves the Ea of the corrosion process [156]. In all the cases it is observed that the values derived from the Arrhenius plot and the equation are found to be the same. The adsorption enthalpy and the

adsorption entropy were computed by the following Eqs (13) and (14).

$$\Delta H_{ads}^0 = E_a - RT, \tag{13}$$

$$\Delta S_{ads}^0 = \frac{(\Delta H_{ads}^0 - \Delta G_{ads}^0)}{T},\tag{14}$$

the values of  $\Delta H^{0}_{ads}$  are positive, signifying the endothermic reaction nature signifying that an increase in temperature promotes the corrosion process [157]. And the  $\Delta S^{0}_{ads}$  values are also found in all tested extracts are positive, verifying that the "corrosion process" is entropically favorable [158].

Generally, the inhibition efficacy of this extracted inhibitor improved with the rising inhibitor level but reduced with rising temperature. In the case of *Cassia alata* leaves the inhibition efficacy value is raised with the rise in temperature [87]. Therefore, the inhibitor efficacies are temperature dependent and it is being chemically adsorbed at higher temperatures. This is mainly owing to the molecule's active adsorption on the surface of the metal being greater than the desorption process. Green inhibitors have characteristics that are comparable to non-green inhibitors. The majority of the eco-friendly inhibitors adsorb on a metal surface using chemical and physical adsorption at room temperature. On extensive exposure to the eco-friendly inhibitor in the direction of the corrosive environment, the inhibitor increases or decreases its efficiency during the progression of corrosion inhibition. The progression of the influence of augmented time on the inhibitor molecules on the metal surface occurs predominantly with a physical interface.

The polarization measurements suggested that these extracted ark from the different parts from the plants acted as mixed type inhibitors [36–40,44,45,50,51,53–55,59,69,75–79,81,89,90,92,93,99,105,110,114,118,120,121,123,125,126,130,133,141,142]. Tafel polarization graph shows all tested extract inhibitors are observed decrease in the corrosion rate, which could be elucidated by the changing of cathodic curves to lower current densities values. Except anodic response of corrosion process is slightly with papaya peel extract [55].

Polarization data showed that the *curry* leaves extract operated as an anodic type inhibitor at lower contents of the inhibitor and as a mixed type at greater inhibitor contents [61]. The displacement in corrosion potential is higher than  $\pm$  85 mV with respect to blank corrosion potential, then the inhibitor could be deemed particularly as an anodic or cathodic type. In the current studies, the greatest positive displacement for aluminum in sulfuric acid was more than 85 mV. This finding suggests that inhibitor molecule elements may operate as anodic types, bringing the anodic process under control [47]. The curves of potentiodynamic polarization, clearly examine that the values of E<sub>corr</sub> moved to more negative potential with the rise in green coffee bean concentration [96], few scientists observed cathodic type inhibitors [55,65,66,80,81,87,117].

The Tafel polarization graphs of aluminum in hydrochloric acid solution, in the absence and presence of diverse concentration of *Calotropis gigantean* leaves extract, are presented in Figure 2. The values of corrosion current densities in the presence ( $2.76 \mu$ A/cm<sup>2</sup>) and absence ( $203.0 \mu$ A/cm<sup>2</sup>) of inhibitor were obtained from the graph, the maximum inhibition efficiency (98%) was observed at 1.25% inhibitor concentration. Addition of the *Calotropis gigantea* leaf extract to acid solution affected both the cathodic and anodic parts of the curves. *Calotropis gigantea* extract, influenced both the anodic dissolution of aluminum and the generated hydrogen gas at the cathode indicating that the extract behaved as mixed-type inhibitor. The decrease in the observed limiting current with increasing

*Calotropis gigantea* concentration indicated that the anodic process is controlled by diffusion. From the polarization figure it was noted that the curves were shifted towards the lower current density region and  $\beta$ a and  $\beta$ c values did not showed any significant change. While the corrosion potential with *Calotropis gigantea* was slightly negative –986 mV, then the without inhibitor observed –958 mV [54].

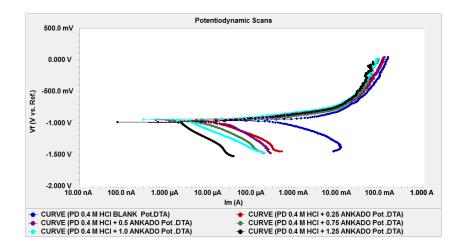


Figure 2. Polarization curve for *Calotropis gigantea* leaves extract in HCl.

EIS is the best method to provide data about the interface's capacitive and resistive behavior as well as assess the influence of extracted compounds on aluminum in acid media. EIS is noted and exhibited by the "Nyquist plot" and, contains two constants; an inductive time constant at lower rates and a capacitive time constant at higher rates. In the EIS a small diameter is noticed in the uninhibited system while the content of inhibitors rises, a diameter becomes greater because of rising resistance. The time constant of capacitive initiates because of the charge transfer mechanism created on moreover the electron conduction via the direct electron transfer or surface film on the surface of the metal. The 1<sup>st</sup> time constant is described in terms of "electric double-layer" and charge transfer due to the dielectric characteristics of the surface layer [159]. However, due to the adsorbed charged intermediates, an inductive time constant develops [160]. However, many researchers supposed that relaxation "adsorption intermediates" on the electrode surface contain Cl [161], oxygen [162], or inhibitor types [163]. Inductive behaviour could also be seen in the pitted active state, which may be ascribed to salt layer property modulation, surface area modulation, or oxide layer surface redissolution [164], examined extract inhibitors explain that aluminum continues to dissolve through the "charge transfer" process on the absorbed inhibitor aluminum surface [165]. The polarization resistance may be measured from the Eq (6). Both  $R_p$  and  $R_{ct}$  values rise considerably with the addition of tested extract, which elucidates about slower corrosion rate of the electrode process in the existence of inhibitors. The Value of R<sub>p</sub> was raised, and there was a drop in the C<sub>dl</sub> values. Therefore, the efficient corrosion resistance was noted to be allied with the higher R<sub>p</sub> value and the lower C<sub>dl</sub> value. The C<sub>dl</sub> is described as an "electrical capacitor" when deemed between the surface metal charge and the solution. In most of the cases observed in the bode spectrum, 2-time constants are apparent, such as a middle frequency and low-frequency time constant. The middle frequency time constant accredited to the "capacitive" behavior of the air formed layer covering the microscopic aluminum surface whereas the lowfrequency connected to the inductive behaviour escorted with the impedance decomposition with frequency decreases consistently to the adsorbed species relaxation process within the oxide layer covering the electrode surface [111]. The inhibitor particle adsorbs on the surface of the metal, reducing its electrical ability by repositioning water molecules as well as adsorbed ions on the surface, as shown by the production of a protective coating on the electrode surface [166].

SEM method provides a pictographic depiction of the metal surface. To comprehend the type of the surface layer in the inhibitor's absences and the presence and extent of the corrosion of aluminum products and their alloy, the SEM micrographs of the surface are studied [167]. The results indicate that the surface is enclosed by a thin film of inhibitors which efficiently controls the aluminum metal dissolution by corrosion agents. The above outcomes are consistent with the explanation made by [43,53,55,62,65,70,75–77,79–81,85,98,114,117,123,125,126,130,133].

There are few researchers who used additives (KI, KBr, KCl) in the inhibition process. The "synergistic parameter" (S) was assessed using the connection provided by Armaki and Hackerman, and described elsewhere [168].

$$S = \frac{1 - I_{A+B}}{1 - I'_{A+B}},\tag{15}$$

$$S = \{1 - I_A - I_B + I_A I_B\} / (1 - I'_{A+B}),$$
(16)

where,  $I_{A+B} = I_A + I_B$ ;  $I_A$  and  $I_B$  indicate the inhibition efficacies of ion-additives and green inhibitors when used alone and  $I'_{A+B}$ =the "inhibition efficiency" of co-employment of 2 inhibitors. The following conclusions may be derived from the S value obtained: if S is greater than 1: the two inhibitors function synergistically; if S is less than 1: the 2 inhibitors act antagonistic; and if S + 1: molecules that operate as inhibitors don't interact with one other. The values of S for (green inhibitors + ion-additives) were assessed and observed to be higher than unity, thereby 2 inhibitors act synergistically [60,68,82,91,138]. The process of synergism could be conceptualized as follows: the active elements of extracts are first adsorbed onto the metal surface where the ion additives were already adsorbed through coulombic attraction. This inhibits corrosion by stabilizing the deposited ions and raising the surface coverage of the metal surface previously covered. When aluminum-ion surface bonds were formed during extraction, their adsorption reduced aluminum's positive charge and allowed the extract's active constituents to be more easily absorbed [169].

#### 4. Conclusions

This review paper summarizes research on aluminum corrosion and its alloys in various acid solutions utilizing a range of natural chemicals that have been published over the last several decades. Plant extracts were by far the utmost examined natural occurring products. A range of solvents was utilized for the extraction, mainly seeds, stems, and leaves of the respective plants. Usually, green corrosion inhibitors are outstanding inhibitors under a diversity of corrosive environments for the aluminum alloy. The non-poisonous and biodegradability are the most important advantages of these eco-friendly inhibitors. Although, they have lots of performance boundaries. However, many articles are witnessing the "green inhibitors" as potent applicants against corrosion in various environments; more research attempts are required to employ the green inhibitors extensively at an industrial level.

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#### **Conflict of interest**

The authors have no conflicts of interest to declare.

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