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PLANT EXTRACTS AS CORROSION INHIBITORS FOR ALUMINUM IN ALKALINE AND IN BOTH ACIDIC AND ALKALINE ENVIRONMENTS - REVIEW II

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ABSTRACT. As a subject of using plant extracts as inhibitors in corrosive environments can easily be founded in many researches in recent years. In this review, studies with various plant extracts used as inhibitors on the corrosion of aluminium in alkaline and both acidic and alkaline environments are given.

1. INTRODUCTION

Corrosion can be defined as the deterioration of metals and alloys as a result of their interactions with their environment. Corrosive products form such as sulfides, oxides, and others (form) during the process. Corrosion negatively affects production and also causes economic losses to a large extent. Because of corrosion many useful properties of metal like malleability, ductility, and electrochemical conductivity are lost. Therefore, it is an undesirable event and is tried to be largely eliminated. There are various methods to prevent corrosion, one of them is the addition of chemical compounds called inhibitors. Inhibitors are organic or inorganic compounds that reduce or prevent corrosion by adding small amounts in corrosive environments. There are many publications that synthesized organic or inorganic compounds are highly toxic and harmful to the environment and health [1-11].

Due to hazardous effects, researchers focus their attention on developing cheap, non-toxic, biodegradable, and eco-friendly natural products of plant origin as corrosion inhibitors. The use of plant extracts as inhibitors to prevent or reduce the

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corrosion of metals and alloys has become increasingly common in recent times. Compared to synthetic inhibitors, plant extract-based corrosion inhibitors also cost less, are biodegradable and non-toxic, and are not harmful to the environment and human health. Therefore, eco-friendly corrosion inhibitors known popularly as green alternatives to replace toxic and hazardous chemicals are studied in recent years [12-33].

Aluminium and its alloys are important industrial materials for many industrial applications such as reaction vessels, pipes, electronic devices, buildings, aerospace, household, marine applications and etc because of its formability, electrical conductivity, mechanical strength, reflectivity, and low mass. On the other hand, aluminium has a negative value of the standard electrode potential.

Therefore, it potentially behaves as an anode material for a power source with high energy densities. Although aluminium is considered that it has resistance to corrosion due to the oxide film formed on its surface, the corrosion of aluminium in acidic and alkaline environments is the subject of many studies. In this review, the corrosion inhibition effects of several plants as corrosion inhibitors for aluminium in alkaline medium and both acidic and alkaline media have been summarized.

2. PLANT EXTRACTS AS CORROSION INHIBITORS FOR ALUMINIUM IN ALKALINE ENVIRONMENTS

When the literature is examined, it is seen that the studies with plant extracts, which have an inhibitory effect on the corrosion of aluminum in alkaline environments are less than the studies in acidic environments. Studies with plant extracts are against aluminium corrosion in alkaline media summarized below.

Sheibani determined the inhibition properties of Henna leaves as environmentally friendly corrosion inhibitors for aluminum in an alkaline medium [34]. The maximum inhibition efficiency reported was for extracts of 20 g of powdered Henna leaves per liter. Weight loss tests for a few days showed that the extracts can inhibit efficiently the corrosion of aluminum in NaOH up to 99.8%. The NaOH concentrations were selected from 0 to 1 M. The inhibition efficiency was found to decrease as the corrosive concentration increased while it increased with increasing the concentration of the extract. In NaOH solutions, the decrease in inhibition efficiency with increasing NaOH concentration can be explained by the reaction of NaOH with some inhibitor species in the extract to form inhibition–inactive species. Water extracts of leaves and four commercial Henna brands were found to inhibit efficiently the corrosion of aluminum in NaOH media.

Singh et al determined the stem extract of *Bacopa monnieri* as a corrosion inhibitor of aluminium in 0.5 M NaOH solution [35]. The researchers used weight loss measurements potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results showed that *Bacopa monnieri* stem extract is an effective inhibitor of aluminium in this alkaline medium. According to experimental results, there is a decrease in corrosion rate with increasing extract concentration, however, these values increase with increasing temperature. As the concentration reached 400 mgL^{-1} and 308K temperature, the inhibition efficiency of the extract obtained from the weight loss method was 94% while this value was found 96% from electrochemical polarization results at the same conditions. Potentiodynamic polarization curves proved that the *Bacopa monnieri* stem extract was a mixed-type inhibitor. EIS plots indicated that the charge transfer resistances increase with increasing concentration of the extract. The adsorption model of the extract obeys the Langmuir adsorption isotherm. The corrosion inhibition properties of *Piper longum fruit* extract and *Bacopa monnieri* stem extract in 1 M sodium hydroxide solution were studied by Singh and Quarishi using the weight loss method [36]. It was found that the inhibition efficiency increased with increasing concentration of the extracts. However, the *Piper longum* fruit extract was found to be more effective than the *Bacopa monnieri* stem extract. For example, the *Piper longum fruit* extract showed maximum inhibition efficiency of 95% at an optimum concentration of 400 mgL^{-1} whereas *Bacopa monnieri* stem extract showed maximum inhibition efficiency of 75% at 400 mgL^{-1} at 308K. Both the extracts of *Piper longum* and *Bacopa monnieri* reduce corrosion of aluminium in 1 M alkali medium by adsorption mechanism.

The inhibiting action of *Piper longum seed* extract was reported as the corrosion inhibitor of aluminium in 1 M NaOH solution by Singh et al [37]. The authors used weight loss measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods. The results showed that inhibition efficiency increases with increasing extract concentration. At the highest extract concentration of 400 mgL^{-1}, the inhibition efficiency is increased maximum value of 94%. Potentiodynamic polarization curves indicated that *Piper longum seed* extract was a mixed-type inhibitor. EIS plots revealed that the charge transfer resistance increases with the increasing concentration of the extract. *Piper longum seed* extract inhibits the corrosion of aluminium in alkali media by an adsorption mechanism. The adsorption model is in accordance with the Langmuir adsorption isotherm.

Corrosion inhibition of aluminum in 1 M NaOH solution by *Mesembryanthemum nodiflorum* leaves was investigated by Al Shboul et al using the weight loss technique [38]. The inhibition efficiency was found to increase with increasing the concentration of the extract at 50°C. It was also found that the inhibition efficiency increases with increasing temperature. The maximum inhibition efficiency was determined at a value of 95.1% at a maximum inhibitor concentration of 14 gL-1 at 50°C. The adsorption of the inhibitor molecules was found to be consistent with a physical adsorption mechanism. Different adsorption isotherms such as Langmuir and Temkin were tested to investigate the nature of adsorption. Langmuir adsorption isotherm was found to be suitable to fit the experimental findings. In this study, some thermodynamic parameters such as adsorption-free energy, enthalpy, and entropy were determined from experimental results. In another study density functional theory (DFT) calculations were performed for the *Mesembryanthemum nodiflorum* by Al-Mazaideh et al [39]. The researchers applied on *Mesembrine, Mesembrenone, Mesembrenol,* and *Tortucsamine,* using Gaussian 03 (G03) program with complete optimization of geometries. Quantum parameters and thermodynamic Gibbs function were used to determine the efficiency of the corrosion inhibition of each compound. It can be concluded that theoretical calculations gave a good picture of the *Mesembryanthemum nodiflorum* leaf extract by suggesting that *Messenbrenone* shows the most inhibition efficiency compared to the other compounds because it was low E_{LUMO} that can form a strong interaction with aluminium to act as a cathodic inhibitor. The measured ΔG value for *Nodifflorum* extract at temperature 298K is -11.5 $kJmol^{-1}$ which suggests physical adsorption. Quantum parameters and frontier orbitals together with calculated thermodynamic function ΔG for adsorption show spontaneous physical adsorption of the *Mesembrenone* on aluminium.

The corrosion inhibition of aluminium by *Ipomoea Involcrata* in 1 M NaOH was studied by Obot and Obi-Egbedi using the gasometric technique at 30 and 60 °C [40]. It was found that inhibition efficiency increased with an increase in the concentration of the extract up to 55.0% at 50% (v/v) and decreased with an increase in temperature. The adsorption of *Ipomoea Involcrata* extract on an aluminium surface was in accord with Langmuir adsorption isotherm at studied temperatures. The physical adsorption was proposed from the kinetic/ thermodynamic parameters determined.

The corrosion inhibition properties of *Gossypium hirsutum* L leave extracts and seed extracts were studied by Abiola et al in 2 M NaOH using weight loss measurement [41]. The inhibition efficiency of both extracts increased with increasing concentration of the extracts. The leaf extract of *Gossypium hirsutum* was slightly more effective than the seed extract in reducing the corrosion rate of aluminium in this alkaline medium. For the leaf extracts inhibition efficiency was found 97% while seed extracts showed 94% at the highest concentration. The inhibition efficiency of the aqueous extract of *Garlic* in controlling corrosion of aluminium immersed in sodium hydroxide solution at pH 11 and 12, in the absence and presence of Zn^{+2}, was evaluated by the weight loss method [42]. At pH 11, the extract accelerated corrosion of aluminium in the absence and presence of Zn^{+2}.

Akalezi et al investigated the inhibition efficiency of *Bucolzia coriacea* (BC) and *Cninodoscolus chayansa* (CC) plant extracts as corrosion inhibitors for aluminium pigments using the gas volumetric technique in alkali media [43]. The study results indicated that the extracts inhibited the corrosion process of aluminium pigment leading to an extended latency period compared to that of the uninhibited aluminium pigment. the latency period was found to depend on pH, temperature, stirring rate, concentration, and plant type A linear correlation was obtained between inhibition efficiency and duration of latency for each extract. If the inhibition activities of BC and CC are examined as a function of hydrogen gas output, it is seen that the inhibition efficiency values determined for BC are higher than the values determined for CC. For example, at 40°C temperature and pH 10.5, the efficiency for 100 ml H_2 gas output was determined as 94.9% in BC and 69.4% in CC. Molecular modeling was used to confirm the structure, and electronic reactive parameters of the plant extract in relation to their effectiveness as corrosion inhibitors.

The inhibition efficiency of an aqueous extract of *Hibiscus rosa-sinencis* (white) in controlling corrosion of aluminium at pH 12 has been evaluated by Rajendran et al weight loss method in the absence and presence of Zn^{+} [44]. The formulation consisting of 8 mL flower extract and 50 ppm of Zn^{+2} had 98% inhibition efficiency. Electrochemical impedance spectra results revealed the presence of a protective film formed on the metal surface. FT-IR spectra showed that the protective film consisted of a complex formed between the main parts of the flower extract and Al^{+3}.

Inhibition of aluminium corrosion in 2 M sodium hydroxide solution in the presence and absence of 0.5 M NaCl using *Damsissa* (*Ambrosia maritime*, L.)

extract has been studied by employing different chemical and electrochemical techniques by Abdel-Gaber et al [45]. The chemical gasometry technique showed that the addition of chloride ions or *Damsissa* extract to sodium hydroxide solution decreases the volume of the hydrogen gas evolved. Potentiodynamic results manifested that chloride ions retard the anodic dissolution presence or absence of chloride ion, influencing both the anodic dissolution of aluminium and the generated hydrogen gas at the cathode indicating that the extract behaved as a mixed-type inhibitor. The decrease in the observed limiting current with increasing *damsissa* extract concentration indicated that the anodic process is controlled by diffusion. Nyquist plots present two capacitive semicircles at higher and lower frequencies separated by an inductive loop at intermediate frequencies. A proposed equivalent circuit was used to analyze the impedance spectra for aluminium in alkaline solutions. The results showed that the *Damsissa* extract could serve as an effective inhibitor for the corrosion of aluminium in alkaline solutions. The impedance measurements verified the remarkable stability of the extracts during storage for up to 35 days. *Damsissa* extract was found more effective in presence of chloride ions than in its absence. Inhibition was found to increase with increasing concentration of the extract but decrease with increasing temperature.

Umoren et al investigated the inhibition efficiency of *Gum arabic* for the corrosion of aluminium in NaOH medium [46]. The inhibition properties of *Gum Arabic* have been evaluated using the hydrogen evolution and thermometric methods at 30 and 40°C. The concentrations of inhibitor used were 0.1-0.5 gL^{-1} and the concentrations of NaOH (as the corrosive medium) were 0.1-2.5 M. The experimental results showed that inhibition efficiency increased with an increase in *Gum arabic* concentration and with an increase in temperature. The type of chemical adsorption was proposed for the inhibition and process followed by the Langmuir and Freundlich adsorption isotherms.

Abdel-Gaber et al showed inhibition of aluminium corrosion in 2 M NaOH solution by a package composed of cationic surfactant cetyl trimethyl ammonium bromide and *Lupine* seed extract has been investigated with different electrochemical techniques and chemical gasometry measurements [47]. Potentiodynamic polarization measurements showed that *Lupine* seed extract controls both the anodic dissolution of aluminium and the hydrogen gas evolved at the cathodic sites of aluminium surface. In the electrochemical impedance spectroscopy method, Nyquist plots showed two capacitive semicircles in the high and low-frequency regions separated by an inductive loop at intermediate frequencies. The inductive loop may be explained by the occurrence of adsorbed intermediates on the aluminium surface. The corrosion inhibition findings have been analyzed using different adsorption isotherms. The results showed excellent agreement between the kinetic-thermodynamic model and the Flory-Huggins isotherm. Gasometry measurements showed that the inhibitive effect of the surfactant increases at a composition around its critical micelle concentration. The presence of both the surfactant and *Lupine* seed extract did not indicate synergistic action between them. and electrochemical techniques. It was found that the inhibition efficiency.

The effects of extracts of *Damsissa*, *Corchours itorius* on the corrosion of aluminum in aqueous 0.1 M sodium carbonate (Na_2CO_3) were published by Abd-El-Nabey et al [48]. The authors used gasometry, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques. Gasometry results revealed that the plant extracts retard the alkaline corrosion of aluminium. According to polarization curves plant extracts behave as mixed-type inhibitors. EIS measurements showed that the Nyquist plots consist of a capacitive semicircle followed by an inductive loop indicating that the dissolution process of aluminum occurs under activation control. Inhibition was found to increase with increasing concentration of the plant extracts. Inhibition efficiencies were found at 90.9% and 85.5% for *Damsissa* and *Corchours itorius*, respectively in 1.00 g/ L extract concentration. According to EIS findings, inhibition efficiencies were determined as 90.1% and 80.3% for *Damsissa* and *Corchours itorius* in the same extract concentration.

TABLE 1. Various plant extracts as corrosion inhibitors for aluminum in alkaline media

Extract	**Medium**	**Methods**	**Type of adsorption**	**Maximum inhibition efficiency (η,%)**	**Ref**
Hibiscus sabdariffa	0.5 M NaOH	mass loss, potentiodynamic polarization, EIS	Langmuir Dubinin-Radushkevich	84.68	[49]
Azwain (Trachyspermum captimum)	0.5 M NaOH	weight loss, EIS	Langmuir	94.00	[50]
Chrysanthemum flower	0.1 M NaOH 0.3 M NaOH 0.5 M NaOH	weight loss, potentiodynamic polarization, EIS, SEM	Langmuir	97.00	[51]
Adathoda vasica	1.0 M NaOH	weight loss, Tafel polarization, EIS	Langmuir	79.70	[52]
Aegle marmelas	1.0 M NaOH	weight loss, gasometric, potentiodynamic polarization, EIS	Langmuir	87.60	[53]
Sinopis alba	1.0 M NaOH	weight loss, SEM electrochemical polarization	Langmuir	97.98	[54]

Extract	Medium	Methods	Type of adsorption	Maximum inhibition efficiency (η,%)	Ref
Capparis decidua	1.0 M NaOH	weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), atomic force methods (AFM) computational studies	Langmuir	92.00	[55]
Moringa leaves	3.0 M KOH	weight loss, Tafel plot, electrochemical impedance spectroscopy (EIS), electron microscopy (SEM)	Langmuir	94.44	[56]
Dialium guineense	3.0 M KOH and 3.0 M NaOH	gravimetric and electrochemical techniques	Temkin	95.3 84.6	[57]
Capparis aegyptia	1.0 M NaOH	Weight loss, electrochemical polarization method	Langmuir, Temkin	93.8	[58]

The effect of the extract of *Phyllanthus amarus* leaves on the corrosion of aluminum in 2 M NaOH solution was determined by Abiola and Otaigbe using the weight loss technique [59]. The extract acts as a corrosion inhibitor with 76% efficiency at 20% v/v extract concentration. It has been observed that the inhibition efficiency increased with increasing concentration of the *Phyllanthus amarus* extract. The adsorption of the extract on aluminum surface was in accordance with the Langmuir adsorption isotherm. The inhibitive effect of *Salvia Judica* on aluminium corrosion in 1 M NaOH solutions was reported by Nawafleh et al [60]. The authors used the weight loss method at different temperatures. The temperatures studied were 25, 30, 40, and 50 °C. Extract concentrations were determined from 0 to 10 (as mL). The inhibition efficiency was found to increase with increasing concentration of the extract and decreased with increasing temperature. Some thermodynamic parameters such as activation energy (E_a), variation of adsorption enthalpy (ΔH), variation of adsorption entropy (ΔS), and the variation of free energy of adsorption (ΔG°) have been calculated to explain the adsorption mechanism. The adsorption of *Salvia Judica* was determined as spontaneous and occurred with physical characteristics.

Irshedat et al determined the effect of the extract of *Lupinus varius l* on the corrosion of Al in 1 M NaOH solution using the weight loss technique at a different temperature [61]. It was found that the inhibition efficiency increased with increasing the concentration of the extract and decreased with increasing temperature. The maximum inhibition efficiency was found 93.73% in 100% (v/v) extract concentration at 25°C. Phytochemical constituents in the extract play a significant role in inhibiting action. The adsorption of *Lupinus varius l* extract fits into Langmuir and Temkin isotherm models and a first-order kinetics relationship was obtained from the kinetics data of weight loss measurements. The inhibitive effect of *Solanum trilobatum* leaves extract on the corrosion of aluminium in 1 M NaOH solution was reported by Geetha et al [62]. The authors studied using weight loss, hydrogen evolution, polarization, and electrochemical impedance spectroscopy methods. The inhibition efficiency increases with the increase of extract concentration and up to 94% inhibition efficiency was obtained for 1.5 gL-1 at 30°C. According to the polarization studies, *Solanum trilobatum* leaves extract acted as a mixed-type inhibitor. The adsorption of the extract onto aluminium surface was found to obey Langmuir adsorption isotherm from the fit of the experimental results at all the concentrations and temperatures studied. In this study, kinetics and thermodynamic parameters for corrosion and adsorption processes were also calculated from the experimental results.

Sirajunnisa et al studied corrosion inhibition of aluminium in 1 N NaOH by leaves extract of *Ziziphus jujuba* using chemical and electrochemical techniques [63]. Inhibition efficiency of *Ziziphus jujuba* extract increased with increase in the concentration of the extract and inhibits the corrosion of aluminium at the best concentration of 900 ppm. However, the inhibition efficiency of the extract decreases with an increase in temperature. Electrochemical polarization curves showed that *Ziziphus jujuba* extract as mixed-type inhibitor by inhibiting both anodic and cathodic reactions to the same extent. The adsorption of the extract on the surface of aluminium follows the Langmuir adsorption isotherm. The negative values of adsorption-free energies ($\Delta G°_{ads}$) indicate that the adsorption process is spontaneous and physically adsorbed on the aluminium surface. The surface photographs showed a good surface coverage on aluminium surface after being used with *Ziziphus jujuba* extracted.

Qudah revealed the inhibition effect of *Cleome droserifola* leaves extract on the corrosion of aluminium in 1 M NaOH solution using the weight loss technique as a function of extract concentrations and temperatures at 25, 35, 45 and 55°C [64]. The surface morphology of Al was analyzed using scanning microscopy (SEM) the inhibition efficiencies increase with increasing the extract concentration and were found to be temperature dependent. The plant extract of 4 gL^{-1} at 35°C has the highest inhibition value for the corrosion of aluminium metal with 78.6% inhibition efficiency. Temkin adsorption isotherm was found to fit the data obtained for the adsorption of the extract on the Al surface. According to the SEM findings, the image for the surface of aluminium metal in 11.2 gL^{-1} *Cleome droserifola* extract solution the surface of al metal is smoother than that obtained in the corrosive NaOH medium, due to the formation of a protective layer at the surface of Al.

The inhibition effect of *Tridax procumbens* leaves on the corrosion of aluminium in 0.5 M NaOH medium was shown by Kiruthiga and Rajendran using weight loss and potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques [65]. SEM photographs were used to determine the surface morphology of metal in the absence and presence of the extract. It was found that the inhibition efficiency increased with the increase of *Tridax procumbens* extract up to 900 ppm. The temperature range was selected from 30 to 70°C. The maximum inhibition efficiency of the extract is 93.35% for 2 hours duration at 30 °C for 900 ppm extract concentration. The *Tridax procumbens* leaves extract control both anodic and cathodic reactions by blocking the active sites of aluminium surface and thus the inhibition is a mixed type. The extract inhibits the corrosion of aluminium in 0.5 N NaOH solution by strong adsorption of its chemical constituents on the aluminium surfaces obeys Langmuir adsorption isotherm.

Corrosion inhibition of aluminium in 1 N NaOH by leaves extract of *Senna auriculata* was studied by Sirajunnisa et al using weight loss and potentiodynamic polarization techniques at 30-60°C [66]. It was found that the inhibition efficiency increasing with increase in concentration of S*enna auriculata* leaves extract but decreases with rise in temperature. The maximum protection effect of the extract was assigned as 76.2%. Polarization measurements indicated that the extract acted as mixed type inhibitor. The adsorption of the extract on Al surface follows Langmuir adsorption isotherm. The negative values of free energy of adsorption process $\Delta G°_{ads}$ is spontaneous and physically adsorbed on the aluminium surface. Surface micrographs showed the presence of a good surface coverage on aluminium surface after being added the extract.

Onen and Buba indicated the corrosion inhibition of aluminum in 0.1 M NaOH medium by *Ficus polita (Bush fig)* at 303, 313, and 323 K using the weight loss method and potentiodynamic polarization experiments [67]. The researchers also used Fourier transform ınfrred spectrometer (FT-IR) for determining the surface morphology of aluminum. According to experimental results from both methods inhibition efficiencies increase with increase in extract concentration and decrease with increase temperature. From weight loss measurements the maximum inhibition efficiency was found as 99.03% at 303K temperature while potentiodynamic polarization findings gave this value 96.40% at the same temperature. The increase in the percent inhibition efficiency as well as the surface coverage (ϴ) indicated that the adsorption of *Ficus polita* on the reaction sites of NaOH plays an important role in the adsorption process. The presence of –C=O-and –N=N- etc. groups in the *Ficus polita* was found to have contributed greatly to the inhibition process by interaction with aluminum surface. Adsorption isotherm was in accordance with Langmuir isotherm. The electrochemical findings revealed that the studied compound acts as mixed type inhibitor.

The effect of *Vitex negundo* leaves extract on the corrosion of aluminium in 1 M NaOH solution was determined by Geetha et al using chemical and electrochemical methods [68]. The inhibition efficiency of the extract increased with increase in its concentration and decreased with a rise in temperature. Polarization curves revealed that all concentrations of the inhibitor exhibited mixed type action. Polarization studies demonstrated that *Vitex negunda* leaves extract shows predominant anodic action. Thermodynamic parameters such as adsorption equilibrium constant and free energy of adsorption were determined. The values of standart free energy of adsorption reveal that adsorption of inhibitor on aluminium surface occurred by physisorption mechanism. Adsorption obeys Langmuir isotherm.

An evaluation of the effective performance of seed extract of *Abrus precatorius* on corrosion inhibition of aluminium in sodium hydroxide media at different temperatures has been made by Rajalakshmi et al [69]. Weight loss and polarization measurement techniques were used to determine the inhibition properties of the extract. The weight loss measurements were carried out with varying concentrations of the inhibitor from 2-14%, The experiments were performed at 313, 323, 333, and 343K and in different time intervals were selected as ½ hour, 1 hour, 3 hours, and 6 hours. From the polarization studies the values of corrosion rates decrease with increasing concentration of the extract. From experimental data, maximum inhibition efficiency was found to be 75.2% at 3 hours of immersion in 0.7% inhibitor concentration polarization curves indicating that the inhibitor is a mixed type. Thermodynamic parameters such as ΔG, ΔH, and ΔS were evaluated, and the negative values of ΔG showed that there is a strong interaction between the metal surface and the seed extract of *Abrus precatorius*. The adsorption isotherm of the extract obeyed Langmuir isotherm and it indicates that the seed extract of *Abrus precatorius* is adsorbed on the Al surface thus highly protective oxide film is formed.

Imane et al illustrated the corrosion inhibition properties of *Mentha pulegium essential oil* in 0.1 M Na_2CO_3 using both polarization and impedance techniques [70]. The experiments have been made in different extract concentrations and temperatures. It was determined that the inhibition efficiency values increased with increasing extract concentration. However, these values changed with a temperature inversely proportional. From polarization experiments, maximum inhibition efficiency was calculated as 94.92% while this value was found as 84.47% from electrochemical impedance spectroscopy measurements in 800 ppm inhibitor concentration at 288 K temperature. It was determined that *Mentha pulegium essential oil* acted as a mixed-type inhibitor. The corrosion inhibition occurred by the adsorption molecules onto the aluminum surface by forming weak bonds. The calculated values of activation energy without and with inhibitor are 21.82 kJ/mol and 68.57 kJ/mol, respectively. The activation energy increase in the presence of the *essential oil of Mentha pulegium* shows that the inhibition was achieved by a physisorption mechanism.

Grishina et al determined the effect of *Flax straw* extract on Al corrosion inhibition in 5 M KOH solution using weight loss method, electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods [71], besides scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy techniques (FT-IR) were applied (FT-IR) to determine the surface morphology of aluminium. If *Flax stra*w extract was added (3 vol %) to the 5 M KOH medium it acts as a mixed-type inhibitor for Al corrosion. The electrochemistry of Al in the presence of a *Flax straw* extract in the alkaline solution, the effect of the extract on the Al morphology and surface film formed, and the corrosion inhibition mechanism were investigated. Furthermore, the Al-air battery discharge capacity determined from a cell that used the *Flax straw* extract in the alkaline electrolyte is substantially higher than that with only a pure alkaline electrolyte. An increase of the *Flax straw* extract concentration in the alkaline medium from 1 to 3 vol % reduces the Al corrosion rate, however, the reduction of the inhibition efficiency is reduced as the concentration of the *Flax straw* extract increases. The formation of the protective layer on the al surface exposed in the Flax straw extract in an alkaline solution supported by the EIS and FT-IR spectroscopy. Furthermore, the Al-air battery discharge capacity determined from a cell that used the *Flax straw* extract in the alkaline electrolyte is substantially higher than that with only a pure alkaline electrolyte. An increase of the *Flax straw* extract concentration in the alkaline medium from 1 to 3 vol % reduces the Al corrosion rate, however, the reduction of the inhibition efficiency is reduced as the concentration of the *Flax straw* extract increases. The formation of the protective layer on the al surface exposed in the *Flax straw* extract in an alkaline solution supported by the EIS and FT-IR spectroscopy.

Hamdou et al published the inhibition properties of *Ricinus communis* oil against aluminium corrosion in 0.1 M Na_2CO_3 medium [72]. The authors used potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The corrosion efficiency increased with the increase of the concentration of the inhibitor while it decreased with the rise of temperature. The maximum inhibition efficiency of *Ricinus communis* oil was found 88.17% at 1800 ppm inhibitor concentration. According to the results of polarization curves *Ricinus communis* oil is considered a mixed-type inhibitor. The values of the activation energy showed that the inhibition occurred by physisorption.

Onen et al investigated aluminium corrosion using *Piliostigma thonningii* leaf extract as a corrosion inhibitor in 0.1 M NaOH [73]. The researchers studied at 303, 313 and 323 K using gravimetric and electrochemical methods. It was found that the percent inhibition efficiency (%) and as well as the surface coverage increased with the concentration of *Piliostigma thonningii* but it decreased with temperature. The maximum inhibition efficiency was determined 98.73% from weight loss measurements. This value was found 99.06% from potentiodynamic polarization curves. The potentiodynamic measurements revealed that *Piliostigma thonningii* leaf extract is a mixed-type inhibitor,i.e., it affects both cathodic and anodic reactions. The increase in the percent inhibition efficiency indicated the presence of adsorption of the extract on aluminium surface. Langmuir adsorption isotherm was found to be the best explanation of the adsorption behavior of the extract at all temperatures studied.

The corrosion inhibition capacity of *Chrysanthemum coronarium* leaf extract in increasing alkaline aluminum–air (Al-air) battery performance experiments has been published by Pham et al [74]. The authors applied hydrogen gas evolution tests, various electrochemical measurements, and battery performance tests. The surface morphology of al was determined by using scanning electron microscopy (SEM) atomic force microscopy (AFM), Fourier transformed infrared (FT-IR) spectroscopy, and X–ray photoelectron spectroscopy (XPS) applied to disclose the chemical composition of the extract as well as formation mechanism of the protective film on the Al surface. The inhibition efficiency increases as the inhibitor concentration increases. The H_2 evolution tests show the highest inhibition efficiency up to 95.12% at the optimum extract concentration, 4.5 gL^{-1}. The value has been determined 91.09% using the EIS technique. The extract is confirmed as a cathodic type inhibitör by the electrochemical results. *Chrysanthemum coronarium* leave extract adsorbs on the 4 N Al surface through the physisorption mechanism. This adsorption adheres to the Freundlich adsorption model. SEM, AFM. FT-IR and XPS measurements show that the inhibition action of *Chrysanthemum coronarium* leaves extract on the 4 N Al surface is due to the presence of its component molecules. The component molecules in *Chrysanthemum coronarium* leave extract additive interact with each other and adsorbs on the Al surface to form the protective film. This film is durable and reproducible when the battery has a discharge interruption. The presence of this film advances the capacity density of the battery up to 2941.18 $mAhg^{-1}$, which increases three-fold compared to a 4 M NaOH solution. Furthermore, in this study, the electrochemical activity of the Al electrode is improved significantly.

Pham et al reported the effectiveness of *Collard greens* to extract as a potent inhibitor for self-corrosion of aluminum in an alkaline aluminum–air battery using weight loss measurements, galvanostatic discharge tests, and electrochemical techniques [75]. Scanning electron microscopy (SEM), atomic force microscopy (AFM) and Fourier transform infrared (FT-IR) spectroscopy methods were performed to determine the morphology of aluminium. The obtained results reveal that the efficiency and capacity density of the battery was significantly increased by the presence of the extract. The inhibition efficiency reached the maximum values at $2.0gL^{-1}$, about 89.61% and 87.90% from potentiodynamic polarization and electrochemical impedance spectroscopy measurements, respectively. *Collard greens* extract acts as a cathodic inhibitor, and the adsorption mechanism of the extract is in accordance with the Freundlich isotherm. The physical adsorption of the extract on aluminum surface was determined through nuclear magnetic resonance spectroscopy.

Raghavendra et al indicated the inhibition performance of *sapota* leaf extract for aluminium corrosion in a 3 M NaOH medium using gasometric, atomic absorption spectroscopy, electrochemical polarization, and impedance spectroscopy techniques [76]. The gasometric data revealed that four different concentrations of the extract inhibit the Al corrosion and the protection efficiency of the extract varies as with time. The maximum value of efficiency was determined as 88% for $2.0gl^{-1}$ extract concentration in 5 hours. According to Tafel graphs, the maximum protection efficiency is 90% for the same extract concentration and at the same time. Tafel curves indicated that the *sapota* leaf extract species adsorb on both anodic and cathodic regions of aluminium in an alkali medium. The extract blocks the corrosion process by mixed mode. The alternative current impedance spectroscopy results showed that the plant extract inhibits the corrosion process by forming a protective layer on the aluminium surface through an adsorption process. The protection efficiency of sabota leaf extract as the maximum value was found 99.70%. Further, alternative current impedance spectroscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) revealed the protective role of *sapota* leaves on the substrate surface in a 3 M NaOH medium.

The design of the experiment was used by Prabhu et al to study the effect of concentration of inhibition and temperature on the inhibition efficiency using *Coriandum sativum* L extract on pure aluminum (99.6%). In this study, aluminum samples were dipped in 0.5 M NaOH solution at different temperatures without and with extract [77]. The result of these experiments shows that the *Coriandum sativa* L diminished with a rise in the concentration of the extract and increase with an increase in temperature. Likewise, it was seen that the inhibition efficiency decreased with an increase in temperature and enhanced with increase in the concentration of the extract. Response surface methodology (RSM) was used to determine and to investigate the optimum parameters for increasing the inhibition efficiency by use of *Coriandum sativum* L extract as corrosion inhibitör. Otherwise, statical analysis of variance was applied to establish the correlations between predicted and experimental results.

The corrosion inhibitive effect of *Derris indica* leaves extract on aluminium in 1 M NaOH was investigated by Nambiar et al at different temperatures [78]. For this purpose the researchers applied weight loss studies and electrochemical methods such as Tafel polarization and electrochemical impedance spectroscopy (EIS). Surface analyses of the treated and untreated aluminium samples were done by using metallurgical microscopy. The maximum corrosion efficiency was found 60.2% with an optimum inhibitor concentration of 1.2 gL^{-1}. Both weight loss and electrochemical studies confirmed that the presence of the leaves extract formed a protective layer over metal surfaces. According to the electrochemical measurements *Derris indica* leaves extract behaves as a mixed type corrosion inhibitor. In the study, Langmuir adsorption isotherm was found to be the best fit and physical adsorption mechanism was proposed [79].

The effect of *Mimosa pudica* leaves extract on the corrosion of aluminium in 1 N NaOH was studied by Brindha and Venkatraman using weight loss measurements and electrochemical techniques like Tafel polarization and electrochemical impedance spectroscopy [80]. It was found that the inhibition efficiency increased as extract concentration increased with 1.2 gL^{-1} being shown to be the optimum concentration. According to from Tafel polarization technique findings *Mimosa pudica* leaves extract acts as a mixed type inhibitor because there is no significant shift in E_{cor} values. Adsorption of *Mimosa pudica* leaves extract on aluminium surface follows Langmuir adsorption isotherm. The natüre of adsorption was found to be physisorption. Metallurgical microscopic study supports the inhibitive action of the extract.

3. PLANT EXTRACTS AS CORROSION INHIBITORS FOR ALUMINIUM IN BOTH ACIDIC AND ALKALINE ENVIRONMENTS

E. Oguzie determined the inhibitive action of *Sansevieria trifasciata* on aluminium corrosion in 2 M HCl and 2 M KOH solutions using the gasometric technique [81]. The results illustrate that the extract functioned as a good inhibitor in both environments and inhibition efficiency increased with concentration but decrease with rise in temperature. The corrosion process is inhibited by the adsorption of the extract on the aluminium surface following the Freundlich isotherm. The addition of halide salts synergistically increased the inhibition efficiency of extract in the order KCl<KBr<KI. The presence of the extract increased the corrosion activation energy in both media and the adsorption heats gave negative values.

The corrosion inhibition properties of *Gongronema latifolium* extract for aluminum corrosion in both acidic (2 M HCl) and alkaline (2 M KOH) environments have been investigated by Oguzie et al [82]. For this purpose, the researchers used the gas- volumetric technique. The results show that the extract good protects against the corrosion of aluminum in both environments. Inhibition efficiency generally increased with concentration up to maximum values of 97.54% and 90.82% in 2 M HCl and 2 M KOH, respectively. Temperature dependence studies showed that the extract is chemically adsorbed on the aluminum surface all concentrations in 2 M HCl and physically adsorbed in 2 M KOH.

Umoren et al published inhibition properties of the extract from the husk of *Vigna unguiculata* to be an inhibitor for Al in 0.5 M H_2SO_4 and NaOH [83]. However, the metal was found to corrode faster in NaOH than in H_2SO_4. The inhibition efficiency increased with an increase in inhibitor concentration. Inhibition was probably brought about by the adsorption of the inhibitor on the metal surface of alkaloids, and fatty acids constituents of *Vigna unguiculata* on the surface of aluminium. The phenomenon of chemical adsorption is proposed for the calculated values of Ea, Q_{ads} and ΔG_{ads} obtained. The increase in temperature increased the inhibition efficiency of *Vigna unguiculata*, which further confirms chemisorption. Inhibitor adsorption characteristics were approximated by Freundlich and Temkin adsorption isotherms at all concentrations and temperatures studied.

Oguzie et al showed the inhibiting effect of *Ocimum basilicum* extract on aluminium corrosion in 2 M HCl and 2 M KOH solutions, respectively, at 30-60°C [84]. Corrosion rates were determined using the gas volumetric technique and the values obtained in the absence and presence of the extract were used in the calculation of the inhibition efficiency. It was found that *Ocimum basilicum* extract inhibited aluminium corrosion in acidic and alkaline environments. The inhibition efficiency increased with extract concentration and decreased with a rise in temperature, suggesting physical adsorption of the organic matter on the metal surface. These results were corroborated by kinetic and activation parameters for corrosion and adsorption processes evaluated from the experimental data at the temperatures studied. Halide additives synergistically improved the inhibition efficiency of the extract.

The inhibitory effect of *Passiflora vitifolia* leaves extract on the corrosion of aluminium in 1 M HCl and 1 M NaOH by Thilagavathi and Rajalakshmi using mass loss, electrochemistry measurements, and surface analysis co-ordinated with theoretical calculations [85]. Mass loss study results revealed that the percentage inhibition efficiency enhanced with increasing concentration of *Passiflora vitifolia* leaves extract. From polarization measurements of the extract, maximum inhibition efficiency was obtained 85.3% for HCl at 0.7% concentration. From electrochemical impedance spectroscopy measurements of the studied extract on aluminium in 1 M NaOH, maximum inhibition efficiency was found 78.8% at 0.7% concentration. The results showed that *Passiflora vitifolia* extract behaves as mixed-type inhibitor the extract is adsorbed on the Al surface, This adsorption is in accordance with Langmuir isotherm and data obtained suggested physical adsorption as the adsorption mechanism between the extract and aluminium surface. Surface morphology of the Al surface was prevented from corrosion due to the adsorption of the active compounds present in the investigated inhibitor. A quantum chemical study proved that the corrosion efficiency was carried out through the positive adsorption centers by which the Al-extract complex formed on the metal surface.

Emran et al determined the inhibition efficiency of *Cantaloupe* juice and seed extracts in 1.0 M HCl was higher than that in 1.0 M NaOH solutions [86]. In both acidic and basic media, the increase in *Cantaloupe* extracts resulted in an increase in both the inhibition efficiency and the degree of surface coverage. The good corrosion inhibitor properties of *Cantaloupe* extracts are due to the presence of many organic substances. The adsorption of these organic compounds on the aluminum surface makes a barrier for mass and charge transfers. The adsorption of *Cantaloupe* juice and seed extract molecules on an aluminium metal surface in 1.0 M HCl obeys Langmuir's adsorption isotherm. In the case of base media, the adsorption of *Cantaloupe* juice obeys Langmuir's isotherm and Temkin’s isotherm was fit to *Cantaloupe* seeds.

The corrosion behavior of *Cninodosculus chayamansa* extract on aluminum in 0.5 M NaOH and 1 M HCl was published by Okeke et al [87]. The authors determined the corrosion parameters using the gravimetric method. The effects of temperature, concentration, and the addition of KI on the inhibition performance of the *Cninodosculus chayamansa* extract were tested. The experimental results revealed that the extract inhibited corrosion reaction in both the acidic and alkaline environments with the effect becoming more vivid as the extract concentration increased, and weight loss increased as temperature increased. The inhibition efficiency of the extract for aluminium corrosion is higher in the acidic medium compared to the alkaline medium, This case indicates that this extract is more effective in the acidic medium. However, the inhibition efficiency increased with increase in the concentration of the extract for both environments. The addition of KI to the extract significantly reduced the rate of corrosion in the alkaline medium and slightly in the acidic environment. Experimental results were seen to fit the Langmuir adsorption isotherm, this revealed that the organic constituents of the extract chemically adsorbed on the metal/surface interface.

Rachavendra and Bhat determined tha anticorrosive properties of *Areca fat* for aluminium/ test solution interface [88]. The researchers used weight loss and Tafel methods to study the inhibition role of *Areca fat* species on aluminum metal in both acid (0.5 M HCl) and base (0.1 M NaOH) systems. Weight loss studies indicated that loss in the weight of aluminium decreases with increasing the amount of *Areca fat* species, which is due to the adsorption of inhibitor to Al surface and obeys Langmuir adsorption mode. The maximum inhibition efficiency was found 88.468% for 0.1 M NaOH and 83.333% for 0.5 M HCl. The mechanism of inhibition property of *Areca fat* species on the al surface was discussed by kinetic and thermodynamic parameters. The type was further confirmed by Tafel curves. Further, scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques were used in order to confirm the chemical (weight loss) and electrochemical (Tafel curve) results.

The corrosion properties of green color *Arecanut husk* extract as an inhibitor for aluminum metal were determined Raghavendra and Bhar in both 0.5 M HCl and 0.1 M NaOH systems [89]. The protection efficiency of green inhibitor was determined through gravimetric and potentiodynamic polarization (Tafel plot) techniques. The weight loss experiment was made in unstirred and stirred test solutions in order to study the stability of the inhibitory protective film on the aluminum surface. The effect of temperature and time on the adsorption of *Arecanut husk* extracts constituents on the surface of aluminum has been studied both Tafel and Nyquist curves measurement after the stabilization period of aluminum metal in 0.5 M HCl/0.1 M NaOH solution confirmed that the introduction of the extract appreciably decreased the corrosion rate of aluminum. The powder X ray diffraction test was used to study the natüre of green inhibitor and its protective film created on aluminum metal in 0.5 M HCl and 0.1 M NaOH medium. The scanning electron microscopy and atomic force microscopy images confirm that the inhibited aluminum surface is superior compared to uninhibited aluminum surface.

Mardiah et al determined the *Rhodomyrtus tomentosa* leaf extract as an inhibitor of aluminum corrosion in acid and alkaline environments using an immersion test [90]. The gravimetric method was used to calculate the corrosion rate of aluminum without and with the extract. Based on the results of surface studies with scanning electron microscopy (SEM), the level of aluminum corrosion with the addition of inhibitors from karamunting leaf extract can be reduced the corrosion rate of aluminum. The efficiency of using the inhibitör was 73.66% in NaOH solution and 80.78% in HCl solution at the highest inhibitör concentration and immersion time variables. A multiple linear regression model was also used in this study to predict the corrosion rate of aluminum.

Ayuba et al investigated the adsorptive and inhibitive action of *Vitellaria paradoxa* as theoretically in the gas phase and using weight loss in both HCl and NaOH solutions [91]. The plant extract was found to inhibit the corrosion of aluminium with better inhibition efficiency in the acidic medium than in the alkaline medium. The inhibition efficiency of *Vitellaria paradoxa* in both media decreased with increase in temperature, period of immersion and corrodent concentration, but dereased with increasing extract concentration. Thermodynamic parameters such as activation energy (E_a), heat of adsorption (Q_{ads}), entropy of adsorption (ΔS_{ads}) enthalpy of adsorption (ΔH_{ads}) and free energy of adsorption (ΔG_{ads}) for the adsorption predicted as a spontaneous process. Quantum calculations of the adsorptive interaction of the *Vitellaria paradoxa* phytochemicals on Al surface favoured the process of back donation. Data obtained from molecular dynamic simulations corresponds to a stable adsorption structure of the compounds with ester being best adsorbed among thr four selected molecules, while the Fukui indices illustrated that oxygen and carbon are the reactive atoms of the molecules for electrophilic and nucleophilic attacks. Theoetical adsorption energy findings obtained from molecular dynamic simulations confirmed the spontaneity and physical mechanism of the process with figures less than the threshold values required for chemical adsorption. Ayuba et al studied the inhibition of aluminium corrosion in NaOH and HCl solutions in the absence and presence of *Gmelina arborea* extract using thermometric method [92]. The concentrations of HCl and NaOH were selected as 0.6 M, 0.8 M and 1.0 M. *Gmelina arborea* extract acts as a better inhibitor in the acidic environment than in alkaline environment. Tha inhibition efficiency of the extract increased with increase in HCl and NaOH corrodent concentration. The inhibiting effect of the *Gmelina arborea* extract could be attributed to the presence of some phytochemical constituents such as saponin, carbohydrate, tannins, phenolics and flavonoids in the extract which may be adsorbed on the surface of aluminium. Quantative structure activity relationship (QSAR) of the four isolates obtained from the bulk *Gmelina arborea* extract proves the inhibition efficiency of the compounds through the process of back donation. Adsorption and /or binding energy data calculated from molecular dynamic simulations shows all the compounds to obey the physical mechanism. Fukui indices showed oxygen atoms present in the phytochemical substituents as the active sites for nucleophilic and electrophilic attacks. Quantum chemical parameters and molecules dynamic simulations confirmed the spontaneity and adsorption stability of the molecules on the aluminium surface respectively.

4. CONCLUSION

This review article outlines the findings and data from many publications that addressed both acidic and alkaline used for evaluating plant extracts as corrosion inhibitors in both acidic and alkaline environments. Data collected in this review will be an important source for researchers to have an idea about the plant extracts as corrosion inhibitors for metals in corrosive environments.

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