PLANT EXTRACTS AS CORROSION INHIBITORS FOR ALUMINUM ALLOY IN NaCL ENVIRONMENT - RECENT REVIEW

PREETHI KUMARI [1] *AND LAVANYA M* [2*]

[1]*Department of Chemistry, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, INDIA.*
[2]*Department of Chemical Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, INDIA.*

ABSTRACT

In spite of the fact that aluminium and its combinations are regularly used like lightweight materials in a great deal of enterprises, they experience the ill effects of low erosion resistance. Corrosion is a natural phenomena that leads to the deterioration of the metal properties through its electrochemical interaction with the corrosive environment. The costs related to corrosion can be either direct (due to the replacement and maintenance) or indirect. A few strategies and methods have been utilized to mitigate corrosion in aluminium and its compounds under various conditions. Concerns raised over climate and human wellbeing have constrained industries to search for a more appropriate option for the protection of aluminium and its alloys from corrosion. This review emphasizes on the plant extracts applied for aluminium combination consumption restraint in NaCl medium. It summarizes the different techniques used for extraction. Additionally, an understanding to the adsorption isotherms has been discussed in brief.

Keywords: Aluminium alloy, corrosion, plant extract, extraction method, adsorption isotherm, mechanism.

1. INTRODUCTION

Aluminum and its alloys are important industrial materials because of their high technological value and wide spectrum of industrial applications, including aerospace [1], household, marine applications etc [2]. Aluminum is known for formability, electrical conductivity, mechanical strength, reflectivity and light weight. It is economical as compared to other materials of similar features and is abundantly available. In appearance it is a form of silvery tone to approximate gray [3]. Their mechanical properties are due to the addition of alloying elements that, sometimes lead to a decrease in the corrosion resistance [4]. However, localized pitting corrosion is most observed in the regions around the Fe-rich and Cu-rich intermetallic compounds. These intermetallic phases normally reveal distinctive cathodic activity and this turns aluminum susceptible to corrosive attack [5]. Fig 1 displays the different fields influenced by corrosion.

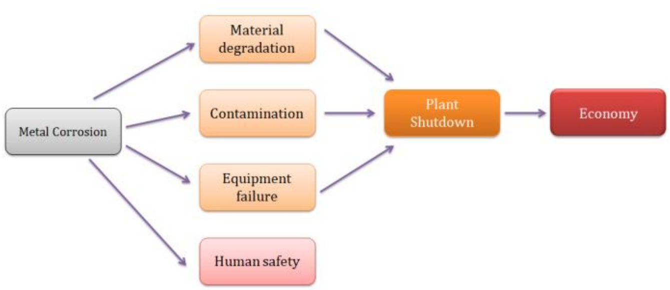

Figure 1. Effects of corrosion on various aspects.

A study carried out proposed that globally, corrosion causes a loss of about 3.4% of total GDP. Nevertheless, by implementation of corrosion prevention strategies in an appropriate manner, the metal degradation cost can be reduced up to 15-35%. Corrosion is a subject of great importance because of its economical and safety related concerns. Therefore engineers and scientists around the world are trying to address this issue [6]. In the light of the aforementioned concerns, alluminum alloys demand protection in various process industries. Chromate conversion coatings (CCC) have been extensively used because of their excellent anti corrosion properties [7]. Additionally, corrosion inhibitors have proved themselves effective in protecting the metals against corrosion with the clear advantages concerning cost, availability, ease of use and high protection efficiency [8].

Corrosion inhibitor compounds normally contain N,S,O,P and other heteroatoms and electron-donating groups [9,10]. They give out electrons and form a defensive film on the metal protecting the material from corrosion. Though organic inhibitors offer good protection efficiency against corrosion they have a complex process of synthesis and is not economically feasible. Moreover they are toxic to the environment [11].Therefore there is a necessity to substitute the toxic and harmful inhibitors with environmentally benign compounds like extracts from plants, biomass wastes and other natural products [12,13].

Green inhibitors

Green chemistry is a division of science whose principles aims at reducing the discharge of hazardous materials into the environment and developing applications of eco-friendly chemicals [14]. The term “green inhibitor” or “eco-friendly inhibitor” is a term referring to a substance that is biocompatible with the nature. Compounds such as plant extracts apparently are biocompatible due to their biological origin [15]. The eco-friendly inhibitors offer a lot of advantages which include being biodegradable, nontoxic, environmentally benign and acceptable, economical, easily available, renewable and safe to apply [16].

An inhibitor is a compound (or a mixture of compounds) added in a very small dosage to the corrosive solution to treat the metal which is known to terminate or reduce the process of metal degradation [17]. Green inhibitors are classified as organic and inorganic inhibitors. Few compounds such as biopolymers, herbal extracts, surfactants, ionic liquids and drugs were used as corrosion inhibitor, in addition few rare earth compounds were also applied as inorganic green inhibitors. The organic inhibitor compounds are applied in acidic conditions, while inorganic inhibitors in the alkanine medium [18]. Among the other green inhibitors, natural plant extracts have become the center of research studies as an environmental corrosion inhibitor. This is accredited to the fact that these compounds have nearly no influence on the ecological system. Besides the source of the material is widespread, so the plant extract is inexpensive [19].

Plant extracts

The application of natural products as anti corrosives can be traced back to 1930’s when *Chelidonium majus* (Celandine) and few other plants were used in sulphuric acid pickling bath. Later, interest in natural products for application as corrosion inhibitors increased considerably and researchers around the globe reported several plant extracts as corrosion inhibitors in various medium [20]. Literature reports the use of phytochemicals in 1960’s when tannins and their derivatives for the protection of steel and iron and few others against corrosion. El Hosary et al. in 1972 stated the use of tobacco from stems, twigs for corrosion protection in aluminum and steel in saline and pickling acids. Plant extracts act as exceptionally rich resources of naturally synthesized chemical compounds [21].The use of herbal extracts as anti corrosion compounds discovered many

**Corresponding author email: lavanya.m@manipal.edu*

constructive aspects such as environmentally benign, economical and renewable [22].The abundant chemical constituents, such as polyphenols, flavonoids, tannins, alkaloids and polysaccharide, bestow plant extract with the prospective of inhibiting the metal corrosion [23, 24]. The extracts from the barks fruits, leaves, seeds and roots of the plants contain organic elements which are frequently composed of N or O atoms [25,26].

Extraction methods adopted for plant products

The extraction methods can be classified into two categories: classical technique and modern technique. The former technique experiences several limitations, which involve the use of excess solvents, a long heating time and time-consuming. These could lead to the deterioration of the bioactive compounds. In most of the instances, use of these solvents was hazardous and poisonous to humans and the environment. Green house gases are released by these organic solvents, intimidating humans, agriculture and microorganisms. Furthermore, the excess solvent generates huge amount of waste by-products. Contrary to these hazardous techniques, eco-friendly approaches like 'green processing', 'green solvents', and 'green product' are encouraged.

The most critical step in the analysis of plants is extraction. Generally, the extraction is a process of separation, where the actives are isolated from the plant. Various parts of the plant produce a variety phyto-chemicals due to the plant matrices. The appropriateness of an extraction method depends on the polar or non polar nature of the target compound [27], sample particle size and the presence of interfering substances. The extraction technique must be cautiously chosen according to the aim of the study. It has an impact on the purity, rate and yield and is subjective to the compound of interest and the degree of purity required [28]. Various extraction methods and the solvents applied are illustrated in Table 1.

Table 1. Extraction methods employed for various plant products

Extraction method	Plant / Herb	Solvent	Reference
Reflux	*Andrographis paniculata*	50% ethanol (v/v)	[28]
Supercritical fluid extraction	P. lobatae root, P. massoniana needle and C. reticulata	supercritical CO2	[67]
solid-liquid extraction	*Andrographis paniculata*	Methanol/ethanol/acetone	[68]
reflux	cactus pear	45% ethanol	[69]
reflux	*Fagopyrum esculentum* Moench	50% (v/v) aqueous ethanol	[70]
Cold and hot extraction	Andrographis paniculata	Chloroform	[71]

Extraction techniques consist of solvent extraction, distillation method, pressing and sublimation as per the principle of extraction. Among these, most often used is solvent extraction method. The natural product extraction advances through the following stages: (1) the solvent penetratiom into the solid matrix; (2) dissolving of the solute in the solvent; (3) the solute diffuses out of the matrix; (4) the solute extracted is collected. Extraction is further facilitated by any of the factors enhancing diffusivity and solubility [29].

General Methods of Extraction of Medicinal Plants

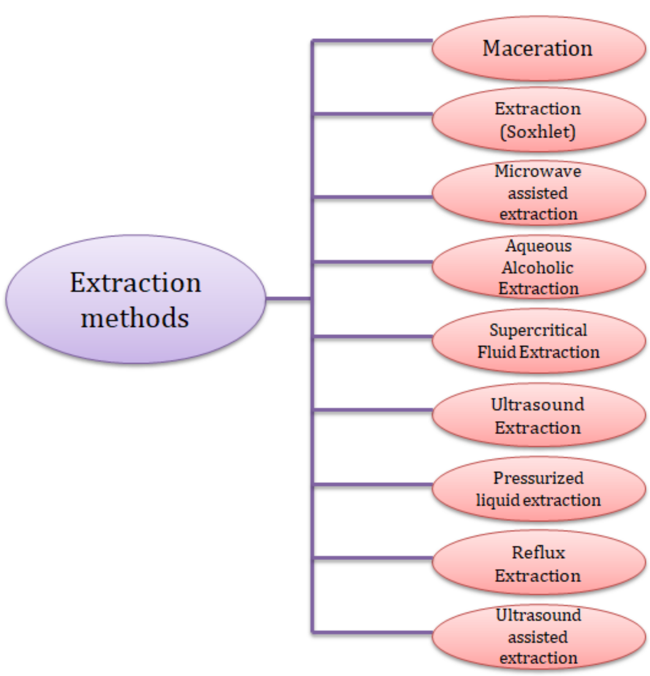

Figure 2. A brief summary of various extraction methods for natural products.

Extraction of natural products demands various extraction methods. Few of them are displayed in Fig 2 [30]. Various extraction methods posses various technical features as well as drawbacks. It is implausible that an extraction technique alone can concurrently congregate all extraction requirements in terms of quality, operation, cost, consumption, and so on. Recently, extraction techniques are employed in combination to assimilate the advantages of different methods [31].

Solvents for extraction

The solvent utilized for medicinal plant extraction is also known as the menstruum. The selection of the solvent is based on the type of plant, part to be extracted, the availability of solvent and the nature of the bioactive compounds. Generally, extraction of polar compounds involves polar solvents, while nonpolar solvents are applied in extraction of nonpolar compounds [32]. Factors to be considered in selecting solvents of extraction are depicted in Fig. 3.

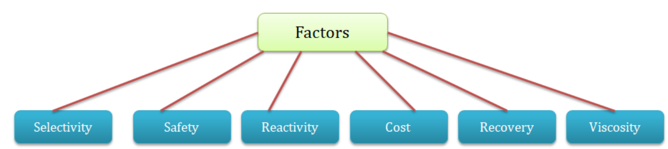

Figure 3. Schematic illustration of various factors affecting the extraction process.

Aluminum alloy corrosion in NaCl Medium

Aluminum is a metal theta is thermodynamically reactive as indicated by the standard electrode potential. Though, the Pourbaix diagram created for the aluminum-water system reveals that aluminum is thermodynamically stable in the pH range between 5 to 8.5. This stability arises from the formation of an oxide layer on the surface with a thickness of about 2–10 nm. This oxide layer avoids further attack on the metal from the corrosive solution, rendering it passive. This passive state can be distorted by several factors. Few important factors include pH, temperature, and chloride content [33].

Corrosion phenomena of aluminum in sodium chloride includes cathodic (1), (2) and the anodic (3), (4), (5) reaction. The anodic reaction leads to the formation of Al_2O_3 film.

$$1/2O_2 + H_2O + e^- = OH + OH^-_{sol} \quad (1)$$
$$OH + e^- = OH^-_{sol} \quad (2)$$
$$Al_s - 3e^- = Al^{3+}_{sol} \quad (3)$$
$$Al^{3+}_{sol} + 3OH^-_{sol} = Al(OH)_{3,S} \quad (4)$$
$$2Al(OH)_{3,S} = Al_2O_{3,s} + 3H_2O \quad (5)$$

At high chloride concentrations bare aluminum will be susceptible to corrosion attack by cl- ions since it lacks protection from oxide layer.

$$Al^{3+}_{sol} + 4Cl^-_{sol} = AlCl_4^- \quad (6)$$
$$Al^{3+}_{sol} + 2Cl^-_{sol} + 2OH^-_{sol} = Al(OH)_2Cl_2^- \quad (7)$$

[34]. In the dilute sodium chloride solution, aluminum hydroxide displays a intense adhesive behavior as compared to the concentrated solution [35].

Aluminum alloy corrosion inhibition in Nacl Medium

The influence of *Laurus nobilis L.* oil on the corrosion mitigation of aluminium and aluminium alloy 5754 in 3% NaCl solution was investigated. A decrease in the cathodic current density was observed on addition of 10 to 50 ppm concentration of oil. The results suggested that aluminium alloy 5754 has better corrosion resistance in the tested solution than pure aluminium, while the oil studied has better inhibition action on pure aluminium corrosion. The study suggested *Laurus nobilis L.* oil as an environmentally friendly alternative [36]. Garlic extract was studied for its corrosion protection efficiency on 1050 aluminum alloy corrosion in 3.5% sodium chloride solution. Garlic extract aided the pit initiation rate on the alloy surface as revealed by the electrochemical noise measurements. However, over time the inhibitor adsorption enhanced thereby reducing the corrosion damage.

Most effective corrosion protection was observed at a dosage of 8mL/L [37]. *Ambrosia maritime*, L. extract was used as corrosion inhibitor to investigate aluminium corrosion in 2 M NaOH along with 0.5 M sodium chloride solution. Electrochemical methods were employed for the analysis. Chemical gasometry revealed the decrease in the evolution of hydrogen gas up on addition of chloride ions/ *Ambrosia maritime* extract to the medium. Both the anodic and cathodic reactions were influenced by the inhibitor in presence and absence of Cl^- ion, indicating that the *Ambrosia maritime* extract behaved as mixed-type inhibitor. Although the inhibitor extract exhibited higher efficiency in presence of chloride ions. Protection efficiency increased both with respect to temperature and concentration [38]. Commercial henna was reported as a potential green inhibitor for 5083 aluminum alloy corrosion in sea water. Lawsone, a major constituent of henna contributed towards corrosion inhibition by forming a layer on the alloy surface. Adsorption process followed Langmuir adsorption isotherm. An important finding was precipitation of the protection layer as time elapsed [39]. Another species of henna, *Lawsonia inermis* was imvestigated for its corrosion behavior on aluminium alloy. Gravimetric methods and electrochemical methods were adopted for the analysis. Solvent employed for extraction was ethyl acetate and methanol. The results suggested from these characterization illustrated that *Lawsonia inermis* extracted in ethyl acetate demonstrates better protection towards corrosion [40].

Leaf

The possibility of using a biodegradable and biologically active extract from Treculia africana (TA) leaves, for corrosion mitigation, for (aluminum alloy) AA7075-T7351 in NaCl (2.86%) medium was assessed using potentiodynamic polarization, electrochemical impedance spectroscopy and gravimetric techniques. Corrosion inhibition on the alloy was predominated by anodic processes, endothermic and spontaneous reactions which obeyed Langmuir, Freundlich and Temkin adsorption models. Bode phase and magnitude plots showed phase angles and slopes increased with increase in inhibitor concentration. SEM micrographs confirmed the inhibiting property of the extract from the increasing surface smoothness [41]. Aluminum alloy in sea water is studied by many researchers. Lawsonia inermis was studied for its corrosion inhibiting property for aluminum alloy in seawater. The extract was characterized by optical study via Fourier transform infrared spectroscopy (FTIR) which proved the existence of carbonyl and hydroxyl groups. Electrochemical methods were employed to study the corrosion behavior of AA 5083 in seawater in the presence and absence of Lawsonia inermis extract. Electrochemical techniques proposed that the addition of the extract has led to the adsorption of inhibitor on the aluminum surface. The adsorption behavior of the inhibitor follow Langmuir adsorption model where the value of free energy of adsorption, is less than 40 kJ/mol indicates that it is a physical adsorption [42].

Root

Extract from Udi plant roots (Terminalia Glaucescens Planch) were investigated for AA 6063 corrosion inhibition in acid (0.3 M H2SO4) and salt (3.5 wt% NaCl) solution. Terminalia Glaucescens Planch extract was applied as an alternative for chemical inhibitors. The inhibition potential of the extract is attributed to the presence of bioactive components such as Tannins, Flavanoids and Keller killani. The corrosion rates both in H2SO4 and 3.5 wt% NaCl decreased up on the addition of the extract [43]. The corrosion mitigation of 7075 AA in (3.5 wt.%) NaCl was studied with berberine. Protection efficiency was found to increase with increasing concentration of the inhibitor. Inhibitor adsorption e on the alloy surface followed Langmuir isotherm. The results revealed that the berberine could serve as a potential inhibitor of the corrosion mitigation of 7075 aluminum alloy in the test medium [44].

Fruit/seeds

Ocimum basilicium seed extract (OBSE) was used as an ecologically safe corrosion inhibitor on 2024 aluminum alloy in sodium chloride solution (3 wt%). The extract revealed an excellent antioxidant activity from the results obtained from DPPH assay. The corrosion protection efficiency increased with the increase in OBSE up to 95.5% at a concentration of 1 g/L. The polarization plots illustrated that corrosion control was achieved through mixed inhibition control. Moreover, the inhibitor adsorption on the surface obeys Langmuir isotherm [45]. AA 5075 –T6 corrosion in 3.5% NaCl was investigated in the presence of Pumpkin seeds (PS). Electrochemical and theoretical studies reported pumpkin seeds as good natural inhibitor for aluminum alloy corrosion. At room temperature (298 K) PS displayed highest protection efficiency of 95%. Besides, PS acted as a cathodic inhibitor. Inhibitor adsorption on AA surface follows the Langmuir isotherm. Surface studies validated the effectiveness of PS by adsorbing on the alloy surface [46].

Phoenix dactylifera L (PDL) fruit juice was evaluated for 7075 aluminum alloy corrosion in sodium chloride medium (3.5%). EIS (electrochemical impedance spectroscopy) and PDP (potentiodynamic polarization) studies were conducted to have an understanding on the corrosion efficiency and behavior of the alloy in the presence of the inhibitor. PDL efficacy increased with the increase in the concentration and it displayed as a cathodic inhibitor. Adsorption mechanism was found to be physisorption and the adsorption pattern followed Temkin model [47]. Inhibitive action of Linum usitatissimum seeds (ELUS) extract was studied. The metal and medium selected for the study was AA2024 and NaCl solution (3.5%) respectively. ELUS was found to effectively inhibit AA2024 corrosion with efficiency ranging from 65 to 82% for the inhibitor concentrations from 80 to 1200 ppm. PDP illustrated that Linum usitatissimum seeds acts as a cathodic inhibitor for the alloy 3.5% NaCl solution. The material; degradation can be mitigated by means of a barrier layer that diminishes electrolyte diffusion towards the alloy surface and/ or formation of an insoluble salt over AA2024 surface [48]. The inhibitor mechanism is a function of the electron density of the molecule and polarizability of the functional groups. Determination of the mechanisms by which plant extracts inhibit corrosion is complex because most of the constituents moderate corrosion reactions in numerous ways, which renders it difficult to assign the credit of corrosion mitigation to any particular constituent. For instance, few of the components may be adsorbed as protonated species and few as non-protonated species, with the principal adsorption mode depending on the existing test conditions at any instant of time. It is worth noting that chloride ions in the medium have a tendency to get adsorbed on the surface in particular, where they facilitate adsorption of inhibitor species (protonated) by creating intermediate bridges between the surface and the inhibitor molecule. Such protonated species are often adsorbed at cathodic sites on the metal surface and hence retard the hydrogen evolution reaction, which is probably responsible for the pronounced cathodic inhibiting effect [49].

General Adsorption mechanism followed by plant extracts

Inhibitor molecules act by adsorbimng on an exposed metal/alloy surface as neutral molecules as a replacement for hydrogen ions adsorbed from the surface of the metal or by dislodgment of water molecules as given by [50] the Eq. (8).

$$\text{Inhibitor}+nH_{ads} \text{-------} \text{Inhibitor}_{ads} + H2\ \text{inhibitor}+nH_{ads}\text{-----}\text{Inhibitor}_{ads}\ H_2E_4 \quad (8)$$

The principal cause for the inhibition capability of a molecule is the presence of heteroatoms. These possess greater electron density and behave as active centres for physisorption or chemical adsorption. Other factors influencing the effectiveness of the inhibitor involve: the structure of functional groups; the presence of π bonds, non-bonding p-orbitals and the electronic properties [51]. The inhibition efficiency of leaves extract as an is mostly related to its capability to get adsorbed on surface of the metal with the adherence [52].

Additional explanation of adsorption mechanism from the study data necessitates assessment of the adsorption modes of the molecule (whether molecular or ionic). The prime adsorption mode will be a function of extract composition, chemical changes to the extract and the surface charge on metal.

A negative surface charge will support the adsorption of cations whereas anion adsorption is preferred by a positive surface charge. Organic inhibitors often interact through two main mechanisms. Namely, chemical and physical adsorption. It has been recommended that physisorbed molecules attach to the surface at the cathodes and basically retard material dissolution by the cathodic reaction whereas chemisorbed molecules shield anodic areas and diminish the inherent reactivity at the sites where they are attached [53]. It is a known fact that the values of (ΔG_{ads}) of the order of 20 kJ mol^{-1} or lower point towards physisorption; those of order of 40 kJ mol^{-1} or higher include charge sharing or transfer to the metal surface from the inhibitor molecules to form a coordinate bond [54].

Adsorption Isotherms

Isotherm equations were utilized to validate the inhibition mechanism that it is truly adsorption. In addition, to ascertain the closest equation that relates the dosage of inhibitors to the adsorbed concentration at saturation. The empirical equations such as hyperbolic, exponential, logarithmic and power are complicated to associate with the given adsorption mechanisms [55]. There are numerous mathematical equations called adsorption models that estimate the adsorbate quantity in the absorbent at a constant temperature, such as Langmuir, Frumkin, Temkin, Flory–Huggins, Freundlich and Bockris–Swinkels. Mostly, the inhibitors follow Langmuir isotherm, some also obey Freundlich and Frumkin isotherms [56]. The intention of the using adsorption isotherms is to illustrate the mechanism of interaction between the surface and the inhibitor [57].

Langmuir isotherms

There are few factors effecting the process of adsorption, but, at the fundamental level, the most extensively studied is temperature. The process of adsorption is generally studied at a given temperature and documented as an adsorption isotherm [58]. The Langmuir isotherm is applicable to homogeneous adsorption where the adsorption of each adsorbate molecule on to the metal surface has equal sorption activation energy [59]. Additionally, the saturation occurs when all of the surface active cites are fully occupied by the adsorbate molecules [60]. The important features of the Langmuir model can be articulated in terms of separation factor or equilibrium parameter R_L that can be obtained from the relationship : $R_L=1/[(K_L*C_0)]$,

Where C_0 is the highest initial concentration (mg/l). The value of R_L indicates whether the type of isotherm is irreversible adsorption ($R_L=0$), favourable adsorption $0< R_L < 1$ unfavorable adsorption ($R_L>1$), or linear adsorption ($R_L=1$) [61].

Freundlich isotherms

The Freundlich model describes the adsorption of metal ions on the heterogeneous surfaces. The Freundlich isotherm is not limited to monolayer coverage alone but also describe multilayer adsorption [62].The linear and non linear forms of the Freundlich model are given by the following [63] equations (9) and (10).

$$q_{eq} = K_F C_e^{1/n} \quad (9)$$

$$\log q_e = \log K_F + 1/n \log Ce \quad (10)$$

where K_F is a constant related to the adsorption capacity, and 1/nF is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the material [64].

Tremkin isotherms

The Temkin isotherm is a two-parameter isotherm. Temkin isotherm model considers the influence of indirect adsorbate/adsorbate interactions on the adsorption process; it is believed that the heat of adsorption of all molecules in the layer reduce linearly as a consequence of increased surface coverage [65]. The linear form of Temkin isotherm model is given by the following Eq. (11).

$$qe=(Rt/b)\ln K_T + (Rt/b) \ln Ce \quad (11)$$

Where b is Temkin constant which is related to the heat of sorption (J mol^{-1}) and KT is Temkin isotherm constant (L/g), R is gas constant (8.31 $Jmol^{-1} k^{-1}$), T is absolute temperature, Ce is concentration of adsorbate at equilibrium (mg g^{-1}) [66].

Challenges faced for sustainability

Merely a tiny portion of actives is included in the plant extracts, therefore, huge amount of plants is obligatory to accomplish the satisfactory inhibition ability resulting in the high cost. Additionally, the process of extraction is too complex to be appropriate for large-scale applications in the industries. One of the alternatives is to verify the essential active components that inhibits corrosion in the plant extracts. Preparation of plant extract plays a crucial role. Every extraction method possesses its own characteristics. Green house gases are released by the organic solvents into the environment, threatening humans and nature. Furthermore, excess solvent usage leads to production of enormous waste by-products. More research is required in order to present efficient and ecologically friendly processes. Plant extracts have exceptional demands in quite a few fields including, cosmetic, pharmaceutical, neutraceutical etc. Consequently medicinal plants cannot be utilized for such applications unless they are copiously available. If corrosion inhibitors could be extracted from the plant waste, it will not only be economical but also be useful to refine the environment. Future studies may focus on the utilization of waste, dead and dried plants.

CONCLUSION

The varied set of studies discussed and summarized advocates the use of plant extracts as corrosion inhibitors for aluminum alloy. Intense research efforts has been put in to tackle the much problematic phenomenon of corrosion. Though plant extract offer several advantages, they suffer certain challenges. Recovery of phytochemicals requires efficient, cheap and environmental-friendly extraction techniques. Many extraction methods have been exploited ranging from conventional techniques to advanced extraction technologies. The extraction methods mostly depend on the choice of solvents and use of agitation and heat to enhance the solubility of the compounds and to improve the mass transfer to the extraction media from the plant matrix.

CONFLICT OF INTEREST

None

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