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Review Article

ALOE VERA AS A GREEN CORROSION INHIBITOR FOR PROTECTION OF METALS AND ALLOYS-A REVIEW

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ABSTRACT

Corrosion is the deterioration of a metal by a chemical attack or reaction with its environment. Aloe vera has the ability to control the corrosion of various metals and alloys, such as aluminum, carbon steel, mild steel, stainless steel, iron, zinc, copper and bronze. Various techniques like the weight loss (WL) method and electrochemical methods such as potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS), have been used to evaluate the corrosion inhibition efficiency (I.E.) of Aloe vera. The protective film has been analyzed by Fourier-transform infrared spectroscopy (FT-IR), UV-visible spectroscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectrometry (EDX) methods. Adsorption of Aloe vera on metal surfaces obeys the Langmuir, Al-Ewady, Frumkin, Freundlich, or Temkin isotherms, depending on the nature of metal and the corrosive environment. A polarization study reveals that Aloe vera can function as an anodic, cathodic, or mixed type of inhibitor.

Keywords: Corrosion inhibition; Aloe vera; Weight loss; Electrochemical methods; SEM.

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1. INTRODUCTION

Corrosion is a natural phenomenon, and its attack on metals has serious negative consequences. It is a constant and continuous problem, often difficult to eliminate completely. Recently, a study revealed that corrosion causes economic losses of about 2.5 trillion US dollars a year, constituting almost 3.4% of the worldwide GDP [1]. As corrosion is associated with economic and safety issues, it should be highly addressed by researchers throughout the world. Metals and alloys are exposed to hostile environments during their industrial usage, including manufacturing, processing, and transportation, which accelerate their degradation. Prevention would be more practical and achievable than complete elimination. Several techniques have been applied in order to reduce the corrosion of metals. The use of inhibitors was one of the most practical and efficient methods for protection against corrosion [2]. A corrosion inhibitor is generally referred to as a chemical substance that, when applied in small quantities to a corrosive medium, reduces the rate of corrosion of a metal or a metal alloy [3]. The application of organic and inorganic inhibitors not only has a toxicity effect on living organisms, but it is also quite expensive. However, due to serious environmental concerns, a lot of research concerning less toxic, cheaper, and more environmentally friendly compounds has been undertaken in the last few years [4-6]. These inhibitor molecules consist of heterocyclic compounds with polar functional groups (e.g., N, S, O, and P) and conjugated double bonds with different aromatic systems. Basically, these substances adsorb on the metal surface to block the destruction reaction with aggressive media. They are both physically and chemically active adsorbate-type substances [7].

The botanical name of Aloe vera is *Aloe barbadensis miller*. It belongs to the Asphodelaceae (Liliaceae) family and is a shrubby or arborescent, perennial, xerophytic, succulent, pea-green color plant. It grows mainly in the dry regions of Africa, Asia, Europe, and America. In India, it is found in Rajasthan, Andhra Pradesh, Gujarat, Maharashtra, and Tamil Nadu [8-9]. The plant has triangular, fleshy leaves with serrated edges, yellow tubular flowers, and fruits that contain numerous seeds. Each leaf is composed of three layers: (1) An inner clear gel that contains 99% water and the rest is made of glucomannans, amino acids, lipids, sterols, and vitamins. (2) The middle layer of latex, which is the bitter yellow sap, contains anthraquinones and glycosides. (3) The outer thick layer of 15–20 cells is called the rind, which has protective function and synthesizes carbohydrates and proteins. Inside the rind are vascular bundles responsible for the transportation of substances such as water (xylem) and starch (phloem) [8]. The name Aloe vera derives from the Arabic word "Alloeh," meaning "shining bitter substance," while "vera" in Latin means "true." [8-9]. It is a very short-stemmed succulent plant growing to 80–100 cm tall, spreading by offsets and root sprouts. The leaves are lanceolate, thick, and fleshy, green to grey-green, with a serrated margin. Aloe vera plant is shown in Figure 1.

Fig.1. *Aloe barbadenis* plant

1.2. Traditional Uses

Aloe vera has been used for medicinal purposes in several cultures for millennia: Greece, Egypt, India, Mexico, Japan, and China. Egyptian queens Nefertiti and Cleopatra used it as part of their regular beauty regimes. Alexander the Great and Christopher Columbus used it to treat soldiers' wounds [8]. The colorless mucilaginous gel from Aloe vera leaves has been extensively used in pharmacological and cosmetic applications. Traditionally, this medicinal plant has been employed to treat skin problems (burns, wounds, and anti-inflammatory processes). Moreover, Aloe vera has shown other therapeutic properties, including anti-inflammatory effects, wound healing, promotion of radiation damage repair, anti-bacterial, anti-viral, anti-fungal, anticancer, anti-diabetic, antiseptic, analgesics and anti-neoplastic activities, stimulation of hematopoiesis, and anti-oxidant effects [9,10]. Aloe vera, as it is commonly called, is organic in nature and can be used in the production of green corrosion inhibitors.

2.1 RESULTS AND DISCUSSION

The corrosion inhibition study of Aloe vera as an inhibitor on various metals and alloys in different media is presented in Table 1.

Table 1. Corrosion inhibition of various metals and alloys by Aloe vera as a green inhibitor.

S/N	Metal /Alloy	Medium + Additive	Techniques used	Findings	Max. I.E. (in %)	Ref. No.
1	Aluminum	0.5 M HCl	WL, PDP, EIS, SEM.	Mixed type of inhibitor, Freundlich adsorption isotherm.	--	11
2	Al Alloy AA8011 &AA8006	3.5 % NaCl	OCP, PDP	Anodic type of inhibitor.	--	12
3	Al- Alloy	10% H_2SO_4 & 3% NaCl	PDP, Cyclic Voltammetry	Cathodic type of inhibitor.	78.35 PDP in H_2SO_4 93.25 PDP in NaCl.	13
4	Bronze B66	3 % NaCl	PDP, EIS, SEM, EDX.	Cathodic type of inhibitor.	97.90 WL, 95.56PDP, 89.36 EIS	14
5	Copper	2M HCl	WL with time and Temperature.	Langmuir adsorption isotherm.	71.1 WL	15
6	Carbon Steel	Rain water + Ni^{+2}	WL, PDP, UV-Vis., FT-IR.	Cathodic-type of Inhibitor.	98.0 WL	16
7	Carbon Steel	Sea water	WL, PDP, EIS, FS UV-Vis., FT-IR.	Anodic-type of Inhibitor.	98.0 WL	17
8	Carbon Steel	Sea water	WL with time, PDP.	Anodic-type of inhibitor. Freundlich and Temkin isotherm.	84.95 WL, 97.05 PDP.	18
9	Carbon Steel	1M HCl	PDP, EIS, EFM, SEM, EDX.	Mixed-type of Inhibitor.	50.4 PDP, 52.15 EIS.	19
10	Carbon Steel	Well water + Zn^{2+}	WL, PDP, EIS, FT-IR	Anodic-type of. inhibitor.	97.0 WL	20

11	Carbon Steel	1M H_2SO_4	WL with time, PDP, EIS, FT-IR.	Mixed-type of inhibitor. Langmuir adsorption Isotherm.	97.69 WL	21
12	Iron	1M HCl	WL with time and Temperature.	Langmuir, Temkin and Frumkin adsorption Isotherms.	83.59 WL	22
13	Mild Steel	1% Wt. NaCl	PDP	Mixed-type of inhibitor	81.81 PDP	23
14	Mild Steel	1M HCl	WL with time and Temperature.	Langmuir adsorption Isotherm.	81.0 WL	24
15	Mild Steel	5 M HCl	WL, PDP, EIS, SEM.	Mixed-type of inhibitor.	97.81 WL, 82.59 PDP.	25
16	Mild Steel	0.5 M H_2SO_4	WL with time, PDP, SEM	Mixed-type of inhibitor, Langmuir adsorption Isotherm.	88.9 WL	26
17	Mild Steel	1N H_2SO_4	WL with Temperature.	----	80.31 WL	27
18	Mild Steel	0.5 M HCl	WL, PDP, EIS, SEM, EDS.	Mixed-type of inhibitor, Langmuir and Al-Ewady adsorption isotherms.	81.00 WL	28
19	Mild Steel	CH_3COOH	WL with Temperature. PDP, EIS.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	82.35 WL, 73.15 PDP, 87.70 EIS.	29
20	Mild Steel	1 & 2 N HNO_3	WL with Temperature.	Efficient inhibitor.	89.94 WL in 2N HNO_3	30
21	Mild Steel	1 M H_2SO_4	PDP, FT-IR.	Mixed-type of inhibitor.	77.43 PDP	31
22	Mild Steel	1-2 N H_2SO_4	WL with temperature.	Langmuir adsorption isotherm.	53.57 WL	32
23	Mild Steel	0.1-0.5M HCl& HNO_3	WL with time and temperature.	Langmuir adsorption isotherm.	77.32 WL	33
24	Mild Steel	1M HCl	WL, PDP, EIS, SEM, AFM.	Mixed-type of inhibitor. Langmuir adsorption Isotherm.	90.0 WL	34
25	Mild Steel	1M HCl	WL with temperature, PDP, EIS.	Mixed-type of inhibitor. Langmuir adsorption Isotherm.	71.66 WL, 70.79 PDP, 77.00 EIS.	35
26	Mild Steel	0.5 M HCl	WL with temperature, PDP, EIS.	Mixed-type of inhibitor, Dubinin-Radushkevich isotherm.	97.0 WL	36
27	Mild Steel	15% HCl	WL with time and temperature.	---	84.0 WL	37
28	Steel Rebar	1M HCl	EIS, SEM.	Mixed-type of inhibitor. Langmuir adsorption	88.5 EIS	38

				Isotherm.		
29	Stainless Steel	Bevarages	WL with time and temperature.	Langmuir adsorption Isotherm.	73.0 WL, 72.91 PDP.	39
30	Stainless Steel	Orange juice	WL with temperature, PDP.	Langmuir adsorption Isotherm.	66.0 WL, 43.2 PDP.	40
31	Stainless Steel	1M H_2SO_4	PDP, FT-IR.	Mixed-type of inhibitor.	--	41
32	Stainless Steel	Milk	WL with temperature, PDP.	Langmuir adsorption Isotherm.	74.0 WL, 52.25 PDP.	42
33	Zinc	2M HCl	WL with temperature, IR.	Langmuir adsorption Isotherm.	67.0 WL	43

Abbreviations: Al: aluminum, AFM: atomic force microscopy, EIS: electrochemical impedance spectroscopy, EDS: energy disperse spectroscopy, EDX: energy dispersive X-ray spectrometry, FT-IR: fourier-transform infrared spectroscopy, FS: fluoroescene spectra, I.E.: inhibition efficiency, NaI: sodium iodide, NaCl: sodium chloride, OCP: open circuit potential, PDP: potentiodynamic polarization, SEM: scanning electron microscopy, UV-vis.: UV-visible spectroscopy, WL: Weight loss.

2.1 Chemical Composition of Aloe vera

Aloe vera contains more than 75 different compounds, including vitamins (vitamin A, C, E, and B12), enzymes (i.e., amylase, catalase, and peroxidase), minerals (i.e., zinc, copper, selenium, and calcium), sugars (monosaccharides such as mannose-6-phosphate and polysaccharides such as glucomannans), anthraquinones (aloin and emodin), fatty acids (i.e., lupeol and campesterol), hormones (auxins and gibberellins), and others (i.e., salicylic acid, lignin, and saponins) [30, 34, 44]. Aloe vera has abundant organic components in which N, S, and O atoms are the main constituent atoms, like aloe-emodin, aloin-barbaloin, anthranol, chrysophanol glucoside, rutin, etc. [35]. The aqueous extract of Aloe vera leaves contains anthraquinones, coumarins, tannins, saponins, steroids, arabinose, resins, galactose, carbohydrates, polysaccharides, and anthra glycosides [32, 45]. Aloe vera gel is the colorless mucilaginous gel obtained from the parenchymaous cell in the fresh leaves of Aloe vera. The aloe vera leaf gel contains about 98 to 99% water. The total solid content of the extracted gel is about 0.66%, and the soluble solids are 0.56% [46]. It contains various active compounds such as salicylates, magnesium lactate, acemennan, lupeol, campestrol, sterol, linolenic, aloctin, and anthraquinones [11, 47]. The gel contains more than 200 different substances. Chief among these are polysaccharides, glycoproteins, vitamins, minerals, and enzymes [48].

2.2. Potentiodynamic Polarization (PDP) Study

Electrochemical polarization measurements were conducted on medium-carbon steel in a 1 M H_2SO_4 solution with and without the addition of a green inhibitor. Five concentrations of 0 ppm, 200 ppm, 400 ppm, 600 ppm, and 800 ppm were added to can be observed from Fig. 4 that the addition of Aloe Vera plant extract changes the anodic (βa) and cathodic (βc) slopes by reducing anodic dissolution and slowing down the hydrogen evolution process, respectively. The corrosive solution, and the obtained Tafel curves are depicted in Figure 2 [21].

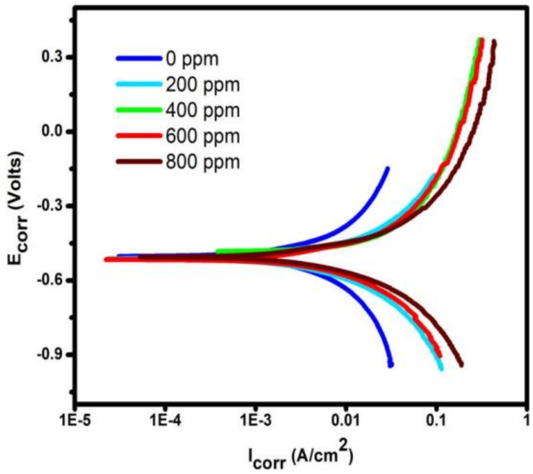

Fig.2. Tafel plot of Aloe vera plant extract at different concentrations on medium carbon steel in 1M H_2SO_4 [21]

However, the considerable change in Tafel curves (anodic and cathodic region) after the addition of green inhibitor specifies that Aloe vera plant extract is a mixed-type of inhibitor [21].

2.3. Electrochemical Impedance Spectroscopy (EIS) Study

The EIS study was conducted to understand the effect of inhibitor concentration on the impedance behaviour of C-steel in a 1 M HCl environment [19]. Semicircles in Fig. 3 shows impedance changes in the presence and absence of inhibitor.

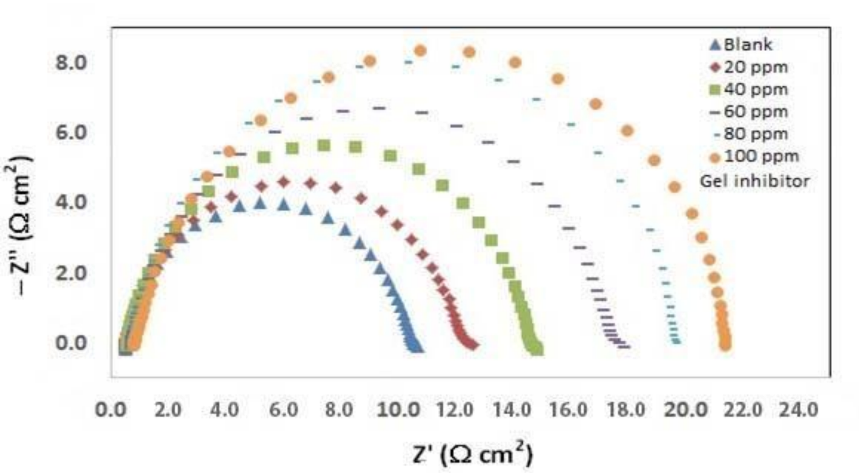

Fig.3. The Nyquist plot for corrosion of C-Steel in 1.0 M HCl in the absence and presence of different concentrations of Aloe vera gel inhibitor at 25 °C [19]

By comparing the semicircle radii of the C-steel in an uninhibited solution and these in the presence of different concentrations of Aloe vera gel inhibitor, it was shown that the real axis intercept at low frequencies in the presence of an extracted Aloe vera gel inhibitor is larger than that in the absence of the Aloe vera gel (blank) and increases with increasing gel inhibitor concentration. The increased impedance of C-Steel corrosion results in an increase in the surface coverage (θ) of inhibitor molecules on the surface of the working C-Steel electrode, which results in an increase in inhibition efficiency. Adsorbed inhibitor molecules form a protective film that isolates the carbon steel surfaces and inhibits both cathodic and anodic reactions at the steel surface [49, 50].

2.4. Fourier-transform Infrared Spectroscopy (FTIR) Study

A few drops of an aqueous extract of Aleo vera (AV) were dried on a glass plate. A solid mass was obtained. Its spectrum is taken and shown in Fig. 4a [16]. The hydroxyl (-OH) group appears at 3431 cm^{-1} and the carboxyl group (C=O) appears at 1631 cm^{-1}. The FTIR spectrum of the protective film formed on the metal surface after immersion in the solution containing 5 ml of AV and 50 ppm of Ni^{2+} is shown in Fig. 4b. The phenolic -OH stretch shifted from 3431 cm^{-1} to 3408 cm^{-1}. The C=O stretching shifted from 1631 cm^{-1} to 1629 cm^{-1}. These shifts confirm the formation of the Fe^{2+}-Aloe vera complex on the anodic sites of the metal surface.

The peak at 1367 cm^{-1} is due to $Ni(OH)_2$ formed on the catholic sites of the metal surface. Thus, the FT-IR spectrum studies lead to the conclusion that the protective film Fe^{2+}-Aloe vera complex formed on the anodic sites of the metal surface and $Ni(OH)_2$ formed on the cathode sites of the metal surface [16]. A few drops of an aqueous extract of Aleo vera were dried on a glass plate. A solid mass was obtained. Its spectrum is shown in Figure 4a [16].

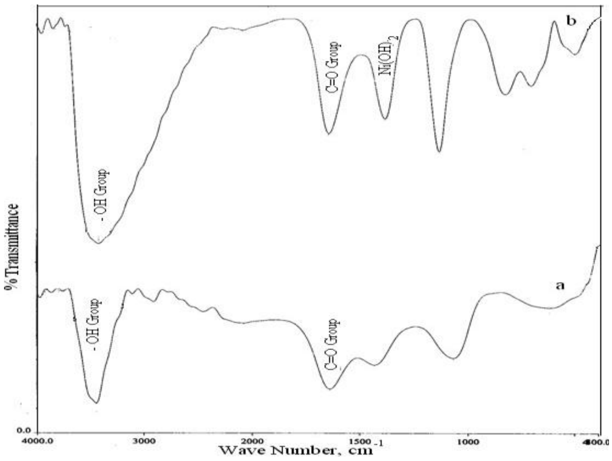

Fig.4. FTIR spectra: (a) pure Aloe vera extract, (b) film formed on carbon steel after immersion in rain water containing 5 ml of AV and 50 ppm of Ni^{2+} [16]

2.5 Scanning Electron Microscopy (SEM) Study

The SEM photographs of Aluminium samples exposed to 0.5 M HCl solution in absence and presence of 4 % and 48 % of Aloe extract for 90 minutes were presented in Figure 5 [11]. Figure 5(a) reveals the microstructure of polished Aluminium before placing it in the test solution. The scan shows that a solid and homogeneous surface is found. Figure 5(b) illustrates that the presence of general and pitting corrosion. Figure 5(c) exhibit the presence of thin porous and protection layer on Aluminium surface contain of numerous pits less than that appears in case of HCl acid alone. Figure 5(d) shows the disappearance of vacuoles (pits) and the formation of an adsorbed film on Aluminium surface due to adsorption of Aloe extract components lead to high corrosion inhibition at this concentration [11].

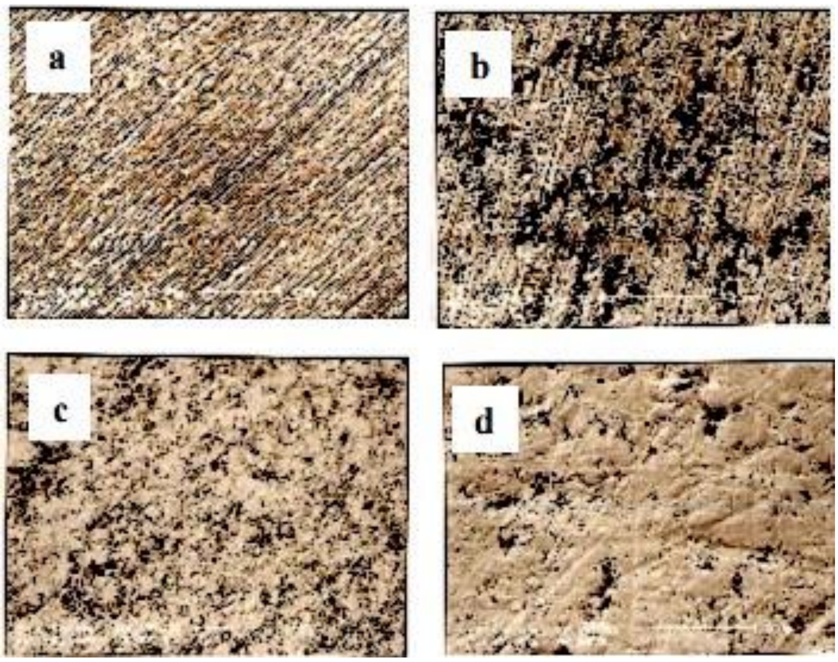

Fig.5. SEM photographs of Aluminium sample, (a) before immersion, (b) after corrosion, (c) in presence of 4% v/v Aloe extract and (d) in presence of 48% v/v of Aloe extract in 0.5 M HCl solution at 30° C

2.6. Mechanism of Corrosion Inhibition

According to Cang et al. [35] Aloe vera have abundant organic components in which N, S, O atoms are the main constituent atoms like Aloe emodin, Aloin-barbaloin, anthranol, chrysophanol glucoside, rutin etc. Structural formulas of compounds isolated from Aloe barbadensis Miller (Aloe vera) is shown in Fig. 6 [51].

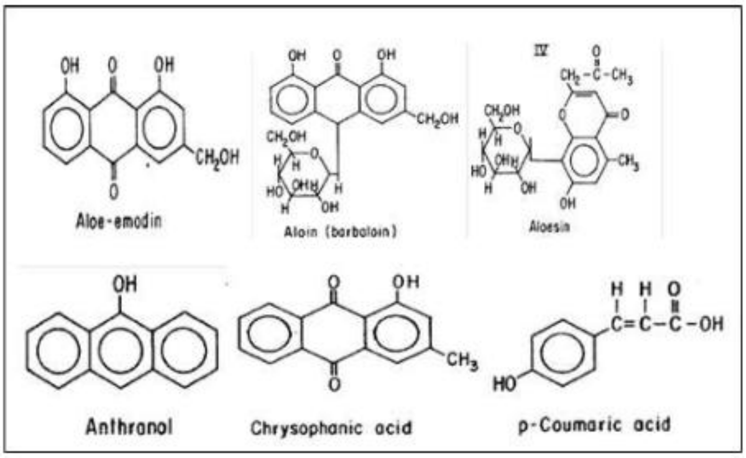

Fig.6. Structural formulas of compounds isolated from Aloe vera

Availability of lone pairs and π electrons in these inhibitor molecules facilitate electron transfer from the inhibitor to the metal, forming a coordinate covalent bond [52]. The inhibition effect of Aloe vera may be due to the presence of these organic compounds in the extract. Hart and James [15] also find that components like folic acid (Vitamin A) and aloe emodin (an anthraquinone) with structures contain electron rich oxygen and nitrogen that could serve as good active ingredients which are responsible for corrosion Inhibition efficiency of Aloe vera.

According to investigation carried out by Sribharathy et al. [17] the active constituent of Aleo vera extract is mannose-6-phosphate. The structure of mannose-6-phosphate is shown in Figure 7 contain phosphate group, hydroxyl group and ring oxygen.

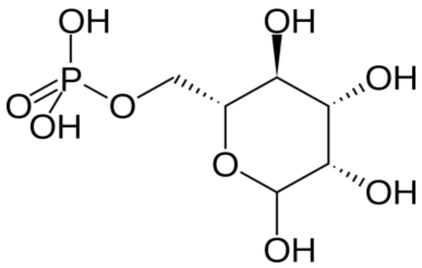

Fig.7. Structure of Mannose -6- phosphate

Studies have shown that Aloe vera contains polysaccharides, steroids, a polygol, organic acids, and essential elements, such as nitrogen, tannins, and antibiotics [18]. The extracted compounds of Aloe vera especially the tannin compound can adsorb on the metal surface and block the active sites on the surface thereby reducing the corrosion rate [40]. The tannin from Aloe vera has been revealed to be adsorbed on the surface of metals, blocking the active sites on the surface, and thereby reducing the rate at which corrosion occurs on the metal [53]. The inhibitive performance reported in most of these plant extracts including Aloe vera is a result of a surface specie possessed by most of these plant extracts which helps in the creation of film over the metallic surface. This creates a barrier between the environment and the metal which prevents corrosion from taking place.

3. CONCLUSION

In this review, various research works on the corrosion inhibition of various metals in different acidic, neutral, seawater, and alkaline media by Aloe vera as a green inhibitor were presented. Langmuir, Frumkin, Freundlich, and Temkin adsorption isotherms were observed. Aloe vera extract behaved as an anodic, cathodic, or mixed-type inhibitor. The maximum inhibition efficiency for Aloe vera was found to be 98.0% (weight loss data). The results obtained from weight loss data were in good agreement with the results obtained from the PDP and EIS methods. A variety of techniques, including SEM, FTIR, AFM, EDX, EDS and others, were used in order to clarify the corrosion mechanism. Some compounds associated with Aloe vera is influence the corrosion inhibition.

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