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Artemisia herba-alba 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. Artemisia herba alba can control the corrosion of various metals and alloys, such as aluminum, carbon steel, mild steel, stainless steel, lead, and tin. Various techniques, such as the weight-loss (WL) method and electrochemical methods, including potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS), have been used to evaluate the corrosion inhibition efficiency (I.E.) of Artemisia herba alba. The protective film has been analyzed by Fourier-transform infrared spectroscopy (FT-IR), Gas chromatography mass spectroscopy (GC-MS), UV-visible spectroscopy (UV-Vis.), and scanning electron microscopy (SEM) methods. Adsorption of Artemisia herba alba on metal surfaces obeys the Langmuir, Frumkin or Temkin isotherms depending on the nature of the metal and the corrosive environment. A polarization study reveals that Artemisia herba alba can function as a mixed-type or cathodic inhibitor.

1. Introduction

Corrosion is defined as the deterioration of substances, especially metals and alloys, resulting from chemical and electrochemical changes with various effects on the environment. Corrosion waste products stop production, cause serious accidents, and result in significant economic losses in various industrial sectors. A recent study indicates that corrosion causes economic losses of approximately $ 2.5 trillion per year, constituting nearly 3.4% of the worldwide GDP (Verma *et al*., 2018). Corrosion can cause disastrous damage to metal and alloy structures, including repair and replacement costs, safety issues, and environmental pollution. Due to these harmful effects, corrosion is an undesirable phenomenon that ought to be prevented (Buchweishaija, 2009). There are several methods for reducing or preventing corrosion, such as anodic and cathodic protection, coatings, and the use of inhibitors.

A corrosion inhibitor is a substance that, when added in small concentrations to an environment, effectively reduces the corrosion rate of a metal exposed to that environment (James *et al.,*2007), (Tebbji *et al.,* 2007), (Zarrouk *et al.*, 2012). Many studies have shown that synthesized organic or inorganic compounds could inhibit the corrosion process (El Ouafi *et al*., 2002), (Praksh *et al*., 2006), (Safak *et al*., 2012), (Atmani *et al*., 2013), (Loukili *et al*., 2023). However, most of these compounds are highly toxic and harmful to the environment and human health. To account for the new environmental protection guidelines, research on the corrosion protection of materials is currently focused on biodegradable products commonly known as green inhibitors. Such inhibitors are non-toxic,

biodegradable, inexpensive, eco-friendly, readily available and not harmful to the environment and human health (Hammouti *et al.,* 1995), (Deepa Rani and Selvaraj, 2011), (Abdel-Gaber *et al.,* 2006), (Umoren and Eduok, 2016). For this purpose, natural products can be considered as the inexhaustible source.

Metals are widely used in human activities due to their excellent mechanical and electrical properties (Verma *et al*., 2018), (Loto and Olowoyo, 2019). In order to preserve the desired state of these metals, their preventive maintenance is a priority. Aluminum is the most used metal after iron because of its low atomic mass, the negative value of standard electrode potential, and corrosion resistance. As a result, aluminum and its alloys play an important role in industry and scientific technologies. In particular, they are widely used in many applications such as car and truck production, electrical engineering, aerospace and aeronautics (Abdallah *et al*., 2016), (Dursun and Soutis, 2014). Carbon steels are extensively utilized in petroleum refineries, fertilizer processing, mining of minerals, building materials, etc. (Fouda and Hamdy, 2013). Mild steel, referred to as low carbon steel, has an enormous number of applications in the Engineering field due to its specific characteristics such as its versatility, cost-effectiveness, weldability, good ductility, recyclability, strength, availability, machinability, malleability, and high impact and tensile strength (Ekeke *et al*., 2020), (Merimi *et al*., 2021). Mild steel is widely used in the industries, especially in the construction, mining, cleaning of boilers, oil well tubes, and metal processing equipment. Stainless steel, which is widely used in metallurgical industries as building material because of its excellent mechanical properties and its cost-effectiveness (Messali *et al*., 2017). Tinplate is a thin sheet iron or steel coated with tin to prevent rusting, used especially to make cans and pots (Bammou *et al.,* 2011). Acid solutions such as hydrogen chloride and sulfuric acids are extensively used in pickling processes of metals which are companioned by significant dissolution of the metals (Hussin *et al*., 2016), (Khadraoui and Khelifa, 2013). Phosphoric acid has been used in many industrial applications. The harmful effect of these acids leads to the use of inhibitors which are judged to be the best method of protection of metals against corrosion (Chauhan and Gunasekaran, 2007), (Khadraoui and Khelifa, 2013).

Description of the Artemisia herba-alba plant

Artemisia herba-alba is a greenish-silver perennial herb growing in semiarid and arid climates, 30 to 50 cm in height and belongs to the family Asteraceae (Talbi *et al.,* 2015), (Chaouche and Haddad., 2023). It is commonly known as “desert wormwood” in English (Behtari *et al.,* 2011), “Armoise” in French, or “Chih” in Morocco (Fakchich and Elachouri, 2021), (Allaoui *et al.*, 2017). Genus Artemisia (Asteraceae family, Anthemideae tribe) comprises more than 300 species (Dob and Benabdelkader, 2006) and is widespread in temperate areas such as South Europe, North Africa, North America, and Asia (Ouachikh *et al.,* 2009), (Salido *et al.,* 2014). Artemisia herba-alba Asso growing wild in semi-arid or arid areas throughout the Mediterranean basin and extending into the North-western Himalayas (Mighri *et al.,* 2010). Artemisia herba-alba grow in arid and semi-arid climates with 100-230 mm annual precipitations In Iran, Artemisia herba alba Asso as medicinal and aromatic plant, is known by the colloquial names of “dermaneh” (Behtari *et al.,* 2011). The vegetative growth of this plant takes place in the autumn; the flowering starts from September to December and basically develops at the end of the summer with many basal, erect and leafy stems covered by woolly hairs (Talbi *et al.,* 2015), (Moufid and Eddouks, 2012). The Artemisia herba alba leaves are characterized by a small silvery appearance, while the flowers are grouped in clusters (Hudaib and Aburjai, 2006). The flowering heads are sessile, oblong and tapering at base. Leaves are strongly aromatic and covered with fine glandular hairs that reflect sunlight giving a grayish aspect to the shrub. The leaves of sterile shoots

are grey, petiolate, ovate to orbicular in outline; whereas, the leaves of flowering stems, more abundant in winter, are much smaller. The stems are rigid and erect. It grows wild in arid areas of the Mediterranean basin. This plant is known as a medicinal and an aromatic plant (Hechiche *et al.,* 2019). Essential oil of Artimisia is characterized by an extraordinary chemical polymorphism (Benabdellah *et al*., 2006). Artemisia herba alba plant is shown in **Figure 1.**

Figure 1. Artemisia herba alba plant (Bouyanzer and Hammouti, 2004)

Traditional uses of Artemisia herba-alba

This plant is known as a medicinal and aromatic plant. *Artemisia herba-alba* is good fodder for grazing animals, mainly sheep, and in the Algerian steppes cattle (Fenardji *et al.,* 1974), (Yashphe *et al.,* 1987), (Mohamed *et al.,* 2004), (Benmansour and Bendiab, 1998). In addition, it is an effective inhibitor of foodborne pathogens, as a natural antioxidant, and is used in potential pharmaceutical applications (Bailey and Danin, 1981), (Jouad *et al.,* 2001), (Hechiche *et al.,* 2019). Artemisia herba-alba species are commonly used as a flavoring agent for coffee (Bailey and Danin, 1981). Herbal tea from this species has been used as analgesic, and hemostatic agents (Laid *et al*., 2008). In addition to that, this herb was used in folk medicine for many years against respiratory disorders, colds, abdominal aches, and kidney sand and stones (Abu-Irmaileh and Afifi, 2003), and for its safety, less toxicity, efficacy, and its availability (Asdadi *et al*., 2020). Furthermore, several species of Artemisia are used in folk medicine, in the treatment of painful menstruation and in the induction of labor or miscarriage (Kalemba *et al*., 2002), as a sedative and an appetizer (Tan *et al*., 1998). It was used for treatment of coughing, intestinal disturbances, as antidiabetic agent (Oberpriele, 2005), (Teixeira da Silva, 2004) and for bronchitis, diarrhea, neuralgias and hyper-tension (Bouhout *et al*., 2022). It is principally used against the treatment of gastric disturbances (Jouad *et al*., 2001). Artemisia species have been used traditionally as a drug for the treatment of gynaecepathy, amenerrhea, bruise and rheumatic disease (Oberpriele, 2005), for the treatment of fungal infections such as tinea, tympanitis, and thrush (Korkmaz and Gürdal, 2002).

Artemisia herba alba is a plant known for its various pharmacological properties such as an anti-inflammatory (Khlifi *et al*., 2013), antifungal (Sami *et al.,* 2010), (Mahmoud *et al*.,1988), anticancer (Tilaoui and Ait Mouse, 2015), antibacterial (Younsi *et al*., 2016), (Mahmoud *et al*., 1988), anthelmintic (Ahmed *et al*., 2020), (Sherif *et al.,* 1987), antispasmodic (Amor *et al*., 2019), (Hechiche *et al.,* 2019), (Yashphe *et al.,* 1987), antiseptic (Hechiche *et al.,* 2019) and antidiabetic (Bouyahya *et*

al., 2021), (Mahmoud *et al*., 1988), antioxidant (Mahmoud *et al*., 1988), anti-venom, nematicidal (Al-Banna *et al.,* 2003), antileishmanial (Hatimi *et al.,* 2001), neurological (Salah and Jager, 2005), hypoglycemic (Jouad *et al.,* 2001), pesticidal (Azaizeh *et al.,* 2007), antimicrobial (against bacteria and fungi) and spasmolytic (Hatimi *et al.,* 2001), (Tahraoui *et al.,* 2007). *Artemisia herba-alba*, in the world, used as pharmaceutical additives, nutraceuticals, and toxicological and anticorrosive agents (Daoudi *et al*., 2023).

2. Methodology

Corrosion inhibition of different metals and alloys in various medium by *Artemisia herba alba* as an inhibitor was shown in **Table1**.

Table 1. Corrosion inhibition of metals and alloys in different media by *Artemisia herba alba* as an inhibitor.

Metal / Alloy	**Medium + Additive**	**Techniques used**	**Findings**	**I.E. max. (in %)**	**Reference**
Aluminium	1 M HCl	WL with temperature, PDP, EIS, SEM, GC, GC-MS.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	91.60 WL, 92.7 PDP, 88.61 EIS	Hechiche *et al.,* 2019
Aluminium	1 M HCl	WL, OCP, PDP, EIS, GC, GC-MS.	Mixed-type of inhibitor.	94.3 WL, 95.0 PDP, 94.3 EIS	Ouchelli *et al.,* 2022
2024 Al-Alloy	1 M HCl	WL with temperature, OCP, PDP, EIS, SEM, LC, HOMO-LUMO.	Mixed-type of inhibitor predomminently cathodic in nature. Langmuir adsorption isotherm.	93.1 WL, 92.4 PDP, 90.4 EIS	Hechiche, *et al.,* 2024
Carbon Steel	1 M HCl	PDP, EIS, AFM.	Mixed-type of inhibitor.	84.8 PDP	Radjai *et al.,* 2018
Lead	0.1 M Na_2CO_3	PDP, EIS.	Mixed-type of inhibitor.	81.64 PDP, 80.54 EIS.	El-Miziani *et al.,* 2015
Mild Steel	1 M HCl	WL, PDP, EIS, SEM, EDS.	Cathodic-type of inhibitor. Langmuir adsorption isotherm.	91.0 WL, 89.0 PDP, 90.0 EIS	Echihi *et al.,* 2021
Mild Steel	1 M HCl	WL, PDP, EIS, SEM, FT-IR, DFT, UV Vis., MD, MS, HOMO-LUMO.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	95.85 WL, 96.98 PDP, 96.17 EIS	Daoudi *et al.,* 2023
Mild Steel	1 M HCl	WL, PDP, EIS, SEM, EDS, DFT, XPS, MDS.	Mixed-type of inhibitor.	90.0 PDP	Berrissoul *et al.,* 2024
Mild Steel	1 M HCl	WL with temperature, PDP, GC, GC-MS.	Cathodic-type of inhibitor. El-Awady adsorption isotherms.	91.0 WL	Boumhara *et al.,* 2012
Stainless Steel	1 M H_3PO_4	PDP, EIS, SEM, EDS, GC-MS.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	88.03 PDP, 85.20 EIS	Boudalia *et al.,* 2019

Steel	0.5 M H_2SO_4	WL with temperature, PDP.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	95.0 WL, 94.0 PDP.	Bouklah and Hammouti, *et al.*, 2006
Steel	1 M HCl	WL with temperature, PDP, EIS.	Cathodic-type of inhibitor. Frumkin adsorption isotherm.	--	Bouyanzer and Hammouti, 2004
Steel	0.5 M H_2SO_4	WL, PDP, GC, GC-MS.	Cathodic-type of inhibitor.	74.0 WL	Ouachikh *et al.*, 2009
Steel	2 M H_3PO_4	WL with temperature, PDP, EIS.	Cathodic-type of inhibitor.	79.0 WL	Benabdellah *et al.*, 2006
X52 Steel	20 % H_2SO_4	PDP.	Cathodic-type of inhibitor. Langmuir adsorption isotherm.	98.29 PDP	Benmenine *et al.*, 2014
304 Stainless Steel	1 M HCl	WL, PDP, EIS, GC, GC-MS.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	82.16 WL, 83.17 PDP, 81.26 EIS	Chaouche and Haddad *et al.*, 2023
Tin plate	0.5 M HCl	PDP, EIS, SEM.	Mixed-type of inhibitor. Langmuir adsorption isotherm.	81.0 PDP, 95.0 EIS	Bammou *et al.*, 2011
Stainless steels: 2205 DSS 2507 DSS	1M HCl & 1M H_2SO_4	PDP	Mixed inhibitor.	1M HCl at 10 g/L 2205 DSS : 79% 2507 DSS: 93 % 1M H_2SO_4 at 5 g/L 2205 DSS:3 % 2507 DSS:38 %	Potgieter *et al.*, 2012.

Abbrevations: AFM: atomic force microscope, **DFT**: density function theory, **EDS**: energy dispersive spectroscopy, **EIS**: electrochemical impedance spectroscopy**, FT-IR**: fourier-transform infrared spectroscope, **GC-MS:** gas chromatography mass spectrometry, **GM**: gasometric method, **HPLC:** high pressure liquid chromatography, **MS:** mild steel, **MC**: Monte Carlo, **MDS**: molecular dynamics simulation, **OCP:** open circuit potential, **PDP:** potentiodynamic polarization**, SEM**: scanning electron microscopy **TM**: thermometric method**, UV-Vis**.: ultraviolet-visible spectrophotometry, **XPS**: X-ray photoelectron spectroscopy, **WL:** weight loss.

Gas chromatography mass spectrometry (GC-MS) study

Ouchelli et al. (Ouchelli *et al.*, 2022) studied corrosion inhibition of Al in 1M HCl solution by *Artemisia herba-alba* as corrosion inhibitor. They carried out GC-MS spectra of *Artemisia herba-alba* as shown in **Figure 2** which indicates various levels of peaks**.** The yields of essential oil extracted from *A. herba-alba*, calculated from air-dried vegetal material (w/w) are to 0.93 ± 0.06%. Chromatographic analysis by GC and GC-MS of *A. herba-alba* essential oil isolated by hydrodistillation identified 79 compounds (**Figure 2)**, accounting for 93.3% of the total oil. The dominant constituents of the oil were chrysanthenone (24.1%), camphor (16.2%), α-thujone (12.8%), 1,8-cineole (9.3%) and β-thujone (4.8%). Camphene, sabinene and α-pinene have so far only been reported as traces. In this work they accounted (2.4%, 1.5% and 1.0%), respectively. Camphor is the most prominent component in the essential oil of Boussaada (49.3%) and Djelfa (32%) of Algeria (Dahmani-Hamzaoui and Baaliouamer, 2010); (Lakehal *et al.*, 2017).

Chrysanthenone is very important in the essential oil of Bordj Bou Arrérridj (43.8%), M'sila (34.3%) (Dahmani-Hamzaoui and Baaliouamer, 2010), southern Spain (36.40%) (Salido *et al*., 2004) and Tunisia (17.37%) (Mighri *et al.,* 2010). This compound could come from the hydrolysis and then the oxidation of cis chrysanthenyl acetate (Giordani *et al.,* 2008). 1,8-Cineole (5.61%) is the main compound in southern Spain essential oil (41.0%) (Salido *et al.,* 2004), Ichemoul in Algeria (Bezza *et al*., 2010) and southern Tunisia (20.00%) (Akrout, 2004).

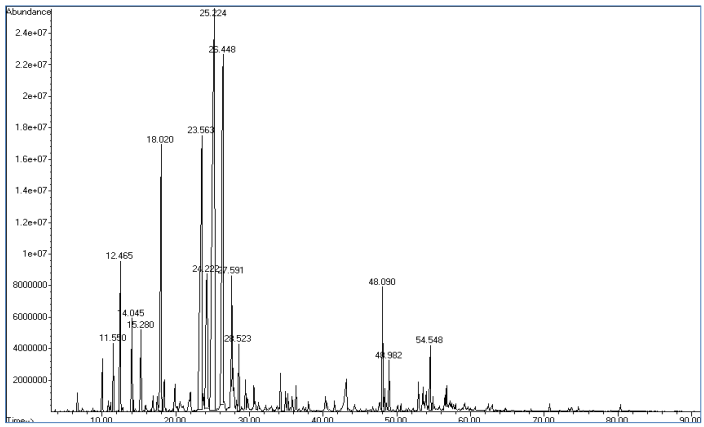

Figure 2. Chromatogram of A. herba Alba essential oil (Ouchelli *et al.,* 2022).

The α-thujone (12.82%) is the major component in Tunisia (44.0%) and Jordan (16.0%) essential oils (Akrout, 2004), (Hudaib and Aburjai, 2006). On the other hand, it is present in variable compositions in the regions of Algeria (1.50 to 35.1%) (Khadraoui and Khelifa, 2013), (Dahmani, 2010). The oil was dominated by ketones (61.6%), followed by alcohols (15.0%). Mono and sesquiterpenic hydrocarbons represented only 8.9% and 4.8% of total oil, respectively. In general, this variation of the chemical composition of A. herba-alba can be attributed to the techniques used for extraction and exogenous factors: the sunshine and the nature and the composition of the soil.

Potentiodynamic polarization (PDP) Study

The polarization curves for MS in 1 N HCl in absence and presence of different concentrations of *Artemisia herba-alba* CHA at 298 K were shown in **Figure 3** (Daoudi *et al.,* 2023). The exploitation of the PDP curves allows for acquiring the inhibiting efficiencies of the biopolymer "cellulose" (CAH) extract from the waste of the *Artemisia herba-alba* plant, in order to exhibit the behavior of the studied inhibitor. **Figure 3** shows that the shapes of PDP graphs remain unchanged in the presence of different concentrations of *Artemisia herba-alba* CHA extract compared to that of the blank, which is accompanied by a decrease in current density from 3.445 mA/cm^2 to 0.104 mA/cm^2 in the absence and presence of 800 mg/L of *Artemisia herba-alba* CHA, respectively. Interestingly, the electrochemical results reveal a remarkable change in the anodic βa and cathodic βc Tafel's law when more and more content of the *Artemisia herba-alba* CHA extract is added, suggesting that the biopolymer effectively retards the iron oxidation and hydrogen ion reduction (Daoudi *et al.,* 2022). Furthermore, Tafel's law is well verified and the corrosion potential E_{corr} is not affected either by the addition of the *Artemisia herba-alba* CHA inhibitor to the blank or by the concentration effect of each CHA.

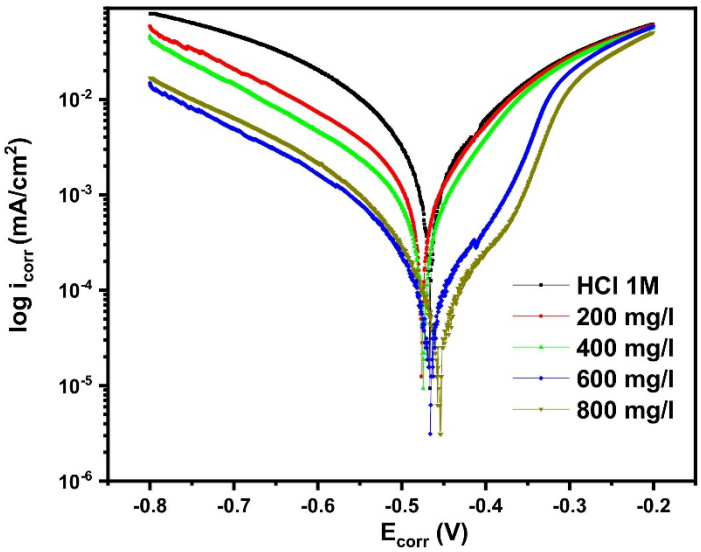

Figure 3. Tafel plots for MS in 1M HCl in absence and presence of *Artemisia herba-alba* extract CHA (Daoudi *et al.,* 2023).

Therefore, it can be concluded that the *Artemisia herba-alba* CHA extract has a mixed characteristic (Hamdouch *et al.,* 2023) and that the corrosive system is controlled by an activation, in which the addition of an inhibitor does not affect the mechanism of the hydrogen evolution reaction (Ansari *et al.,* 2022).

Electrochemical impedance spectroscopy (EIS) study

Echihi et al. (Echihi *et al.,* 2021) studied EIS diagrams for MS in 1 M HCl in the absence and the presence of various concentrations of the methanolic extract of *Artemisia Herba Alba* and Nyquist plots were shown in **Figure 4**.

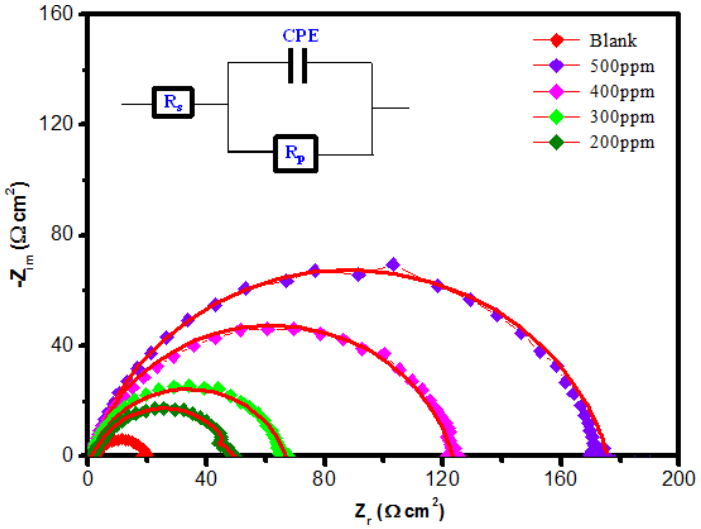

Figure 4. Nyquist curve for MS in 1M HCl solution without and with varying concentrations of MEAHA (Echihi *et al.,* 2021).

The reduction of corrosion inhibition of the MS is largely attributed to the presence of MEAHA, including the adsorption and the film formation on MS, owing to the adsorption of green inhibitor studied and the distance between the substrate surface and a corrosive solution is increased (Tabatabaei majd *et al.,* 2019). As seen in **Figure 4** alone one capacity loop appears in the frequency studies'

impedance spectra, which suggests that the single charger transfer resistance is the main reason indicating in anti-corrosive in the absence and the presence of the methanolic extract of *Artemisia herba alba* green inhibitor. That is possibly related to the charge transfer reaction, the frequency dispersion, the metallic surface inhomogeneity, and the surface roughness (Tabatabaei majd *et al.,* 2019). As such, the higher semicircle implies that the covering film is present in the MS surface. That presence is made possible thanks to the MEAHA adsorption that works to reduce the corrosion process. Also, semicircles' diameter increases with the increase of green inhibitor concentration up to 500 ppm (Salarvand *et al.,* 2017). At higher frequencies range, there is the one which could correspond to the metallic surface corrosion compounds. The other one is at lower frequencies, which may be attributed to the charge transfer process at the substrate/solution interface.

Fourier transform infrared spectroscopy (FT-IR) study

Daoudi et al. (Daoudi *et al.*, 2023) studied the inhibitive effect of *Artemisia herba alba* on the corrosion of MS in 1 M HCl. In this study, *Artemisia herba alba* extract was characterized by using FT-IR spectra was shown in **Figure 5.** To identify the phytochemical functional groups, present in the CHA biopolymer, we used a reliable technique, FT-IR spectroscopy, in order to characterize our recovered bio-organic material. **Figure 5** shows the FT-IR spectrum of commercial cellulose and that of cellulose extracted from the stems and leaves of the plant Artemisia herba-alba. Comparing the two FT-IR spectra, that of the commercial cellulose and that of the biopolymer CHA extracted from the stems and leaves of *Artemisia herba-alba*, we can demonstrate that these spectra are superimposable and that the white solid found at the end of the isolation process used on these stems and leaves corresponds to the biopolymer.

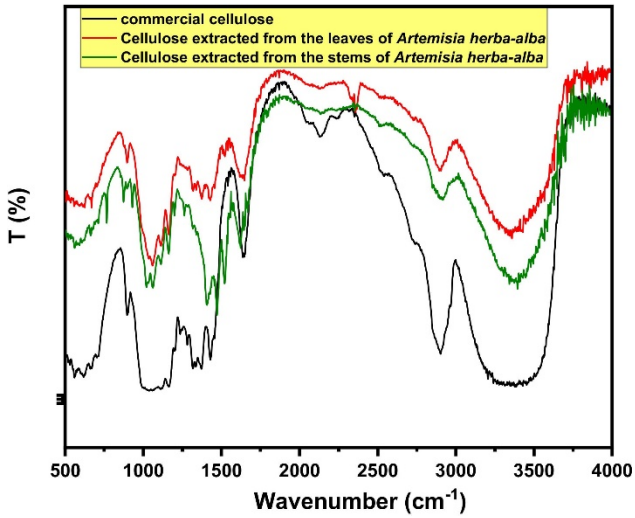

Figure 5. FT-IR spectra of the biopolymer CHA (Daoudi *et al.*, 2023).

By analyzing the spectrum of the extract, we can attribute some present bands to the corresponding vibrators. Indeed, between 3000 and 3600 cm^{-1}, we find the bands of vibrations of elongations of the bonds O–H of the primary and secondary alcohol functions. The vibration of deformation in the plane of function O–H in C_6 is at 1275 cm^{-1}. The vibration band around 2900 cm^{-1} is attributed to the elongation vibrations of the C–H bond. The in- plane deformation vibrations of CH_2 in C_6 (shear, agitation) are at 142 and 1325 cm^{-1}. The antisymmetric elongation vibration of the β-glycosidic C–O–C bond appears at 1163 cm^{-1}. This band is used later to normalize the spectra

as it is expected to undergo no change during the modification steps. Water adsorbed on cellulose appears at 1639 cm^{-1}. However, the absence of a vibration band around 1775 cm^{-1}, which corresponds to the elongation vibration of the C=O bond, confirms the absence of lignin residues on cellulose chains, which shows the total disappearance of all organic encrustations of the wall (lignin) during the bleaching step (Daoudi *et al.*, 2023).

Ultra violet (UV) Visible spectroscopy study

Daudi et al. (Daudi *et al.,* 2023) studied UV-Vis. spectra for MS in 1 M HCl solution with and without CHA extract are shown in **Figure 6**.

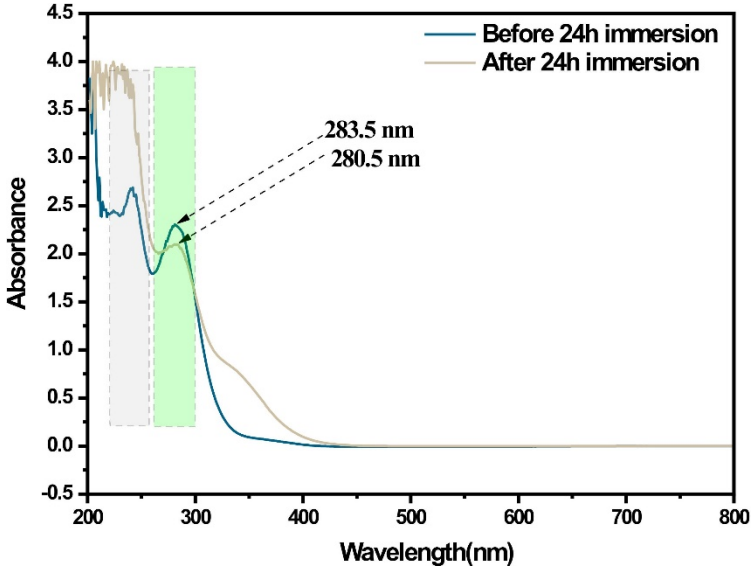

Figure 6. UV-Vis. plots of CHA extract in 1 M HCl medium before and after MS immersion at 298 K (Daudi *et al.,* 2023).

The UV-visible technique was performed to evaluate the possibility of the formation of an iron-CHA complex. **Figure 6** shows the UV-Visible plots of the CHA extract before and after immersion of the mild steel. Before immersion, two intense peaks of wavelengths 283.5 nm and 245 nm are observed. After immersion, two peaks are localized and shifted with respect to the one previously observed, which implies the formation of electrostatic interactions between the ferrous ions and the active cellulose dipoles (Zhou *et al.*, 2022).

Atomic force microscopy (AFM) study

AFM technique supplies photos with atomic or near-atomic-resolution surface topography which able to giving the surface roughness of coupons by the angstrom-scale. AFM is a very higher resolution type of scanning probe microscopy on the order of fractions of a nanometer, more than 1000 times better than the optical diffraction limit (Vera *et al*., 2007). Radjai et al. (Radjai *et al.*, 2018) studied CS surface morphology by using AFM experiments after exposure for 24 h to 1 M HCl in the presence and absence of 400 ppm of Artemisia herba-alba extract (the 2D images) was shown in **Figure 7**. The values of RMS of the freshly polished surface was 9.73 nm. A slight roughness was noticed; a presence of few scratches due to the atmospheric corrosion (Geetha and Rajendran, 2016) or the polishing treatment. The RMS values for the carbon steel surface immersed in 1M HCl solution was 115.94 nm. From this value and the second image, it is easy to see that the carbon steel immersed in hydrochloric acid solution has a greater surface roughness due to corrosion (Li and Meier, 1998). However, in the

presence of the inhibitor, the RMS decreased to 62.87 nm. This reduction demonstrates that the surface becomes smoother (Bertrand *et al.,* 2008) because of the deposition of the inhibitors on the metal surface as shown in the last image. The AFM study shows that the protective film formed on the surface decreases the corrosion rate of carbon steel in the presence of the methanolic extract of *Artemisa Herba Alba* in the hydrochloric solution.

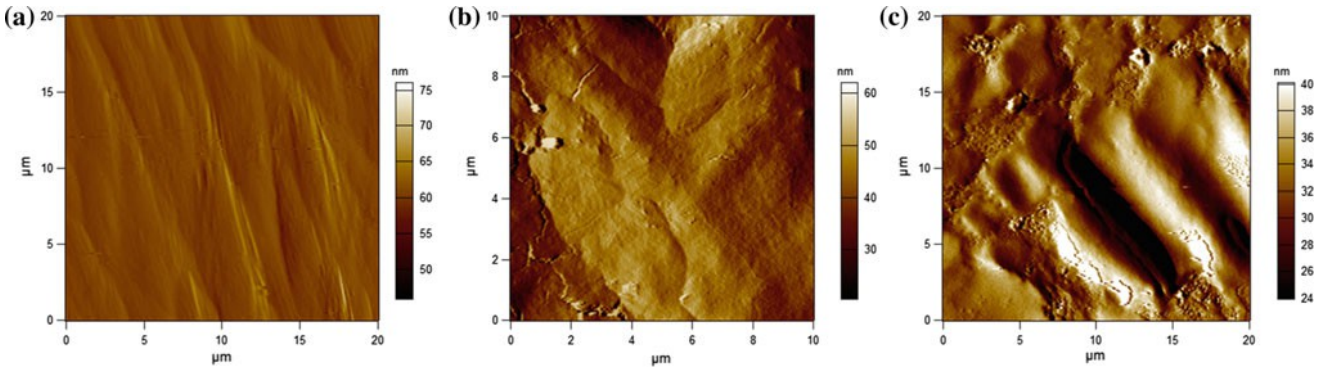

Figure 7. 2D AFM images of carbon steel (a) polished sample (b) immersed in 1M HCl (c) immersed in 1M HCl containing 400 ppm (Radjai *et al.*, 2018).

Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) Study

Echihi et al. (Echihi *et al.*, 2021) studied SEM image of MS samples after immersion in 1M HCl solution without and with AHAME inhibitor is shown in **Figure 8**. So as to get enough information about the properties investigated in the sample of the surface of the steel both in the absence and presence of inhibitor in 1 M HCl, EDX analyses were done. Due to the absence of the extracts (**Figure 8)**, the steel composition becomes hard and gets damaged after being immersed in 1 M HCl solution because of the force of the rapid corrosion.

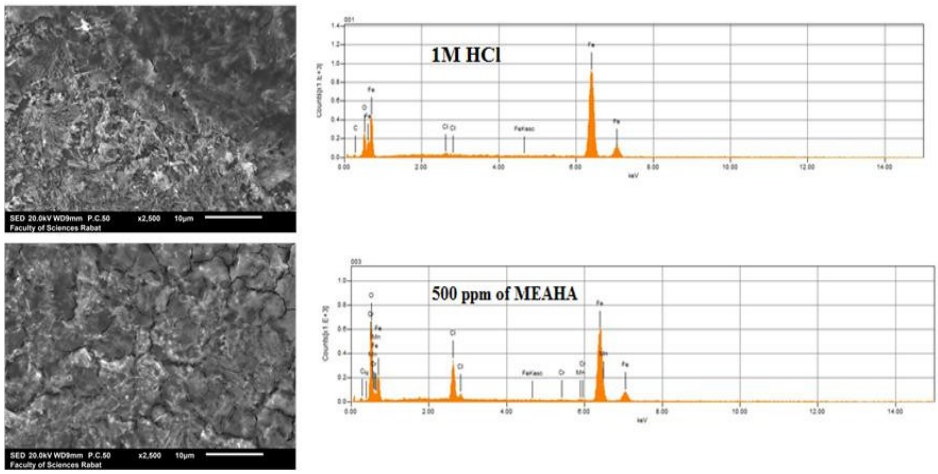

Figure 8. SEM/EDS images of the MS without and with 500 ppm of MEAHA (Echihi *et al.*, 2021).

As a matter of fact, there is a presence of a layer of corrosion product able to absorb fluids (Belghiti *et al.,* 2020). On the contrary, when we add to the aggressive environment 500 ppm of plant extract, this leads to a remarkable decrease in mild steel's corrosive attack (**Figure 8**). As a result, the constitution of corrosion products gets hindered. This blockage leads to a process of changing to an inferior state of the MS. Indeed, as the SEM images demonstrate, there is a sort of improvement at the surface coverage level, and the protective film on the steel surface starts to take shape. The prime reason behind this is associated with the downward change in the interaction between the steel of the surface and the aggressive medium. It is evident from **Figure 8** that the EDX spectrum contained in

aggressive 1M HCl introduces the characteristic and most extreme possible values of particular elements included in the surface of the sample's chemical properties. As such, when the plant extract exists, both the feature peak of nitrogen and enhancement in the intensity level of the peaks of oxygen and carbon become visibly apparent. These are present in the tested inhibitor's chemical constitution (Boudalia *et al.,* 2019).

Density function theory (DFT) study

Daoudi *et al.*, 2023 used Mulliken charge calculation to determine the adsorption centers for inhibitors. **Figure 9** shows the computed Mulliken charges of a few chosen atoms.

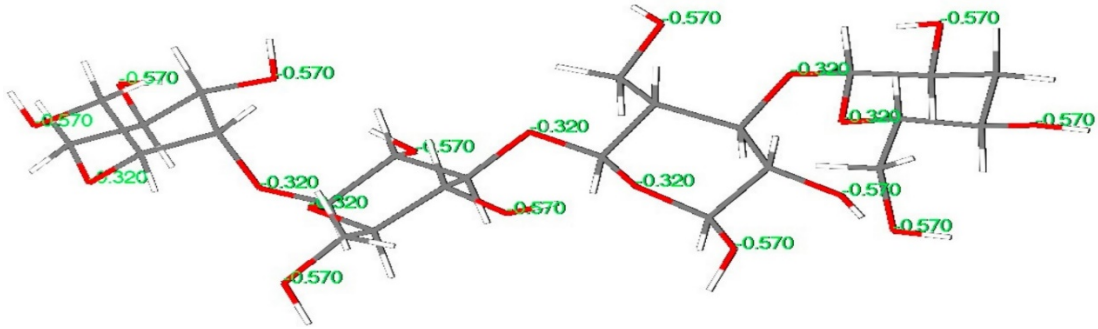

Figure 9. Distribution of the Mulliken charge values of 'O' atoms of the biopolymer molecule CHA (Daudi *et al.,* 2023).

One can see that the heteroatom produces a pronounced surplus of negative charges, thus being able to act as a nucleophilic reagent (Berisha *et al.,* 2021), (Mehmeti, 2022). The Mulliken charges of the atoms, determined for the compound, indicate that the most negative atom is O in red (−0.570) and the latter constitutes the active adsorbent center. Organic chemicals' inhibitory effects often depend on the molecules' ability to adhere to metal surfaces; this adsorption is dependent on the molecules' molecular structures (Dagdag *et al.,* 2019a). The DFT has several advantages and appears adequate for generating the electronic data required for inhibitory activity when compared to other quantum chemical approaches for the assessment of corrosion inhibitors (Haldhar *et al.,* 2021a). For describing the adsorption selectivity of inhibitors, the electron density distributions of border orbitals are crucial (Dagdag *et al.,* 2021). The HOMO and LUMO, the inhibitor's border molecular orbitals, are thought to be intimately connected to the responsiveness of the inhibitor (Berdimurodov *et al.,* 2022a).

The energy of the $\Delta E = (E_{LUMO} - E_{HOMO})$, E_{LUMO}, and E_{HOMO} were taken into consideration as quantum-chemical indicators. E_{HOMO} is frequently related to a molecule's capacity for electron donation. With higher E_{HOMO} levels, inhibition becomes more effective. High E_{HOMO} values show that the molecule has the propensity to give electrons to suitable acceptor molecules that have vacant, low-energy atomic orbitals. E_{LUMO} denotes a molecule's capacity to take electrons (Qiang *et al.,* 2018). The molecule is likely to quickly take electrons from donor molecules, according to the lowest value of E_{LUMO} (Ganjoo *et al.,* 2022). The boundary orbitals of the molecule reveal its chemical reactivity as well as kinetic stability. As adding an electron toward a high-altitude LUMO and removing electrons from a low-altitude HOMO are energetically unfavorable, a large HOMO–LUMO gap predicts great kinetic stability along with low chemical reactivity. The overall electronegativity (χ) is another important reactivity parameter that represents the electron-attracting ability of the molecule. The stronger the electronegativity, the stronger the ability to attract electrons from the metal, resulting in strong interactions and increased corrosion protection.

The inhibition gained via electron donations is described by the fraction of electrons transferred (ΔN). The ability of the metal surface to donate electrons rises with inhibition efficiency (Daudi *et al.,* 2022). The cellulose inhibitor's optimized molecular structures, MEP, LUMO, and HOMO, are shown in **Figure 10**. **Figure 10** shows a visual representation of the density distributions of the HOMO but also LUMO frontier orbitals, the electron density surfaces, as well as the electrostatic potential (MEP) of the cellulose inhibitor forms.

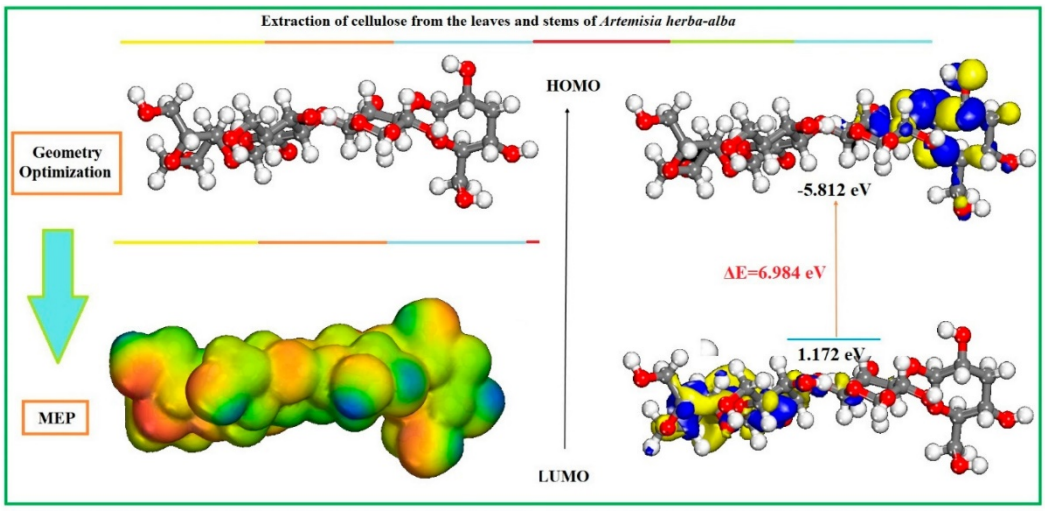

Figure 10. Optimized geometry, MEP pictures, and HOMO and LUMO for the cellulose molecule present in the leaves and stems of *Artemisia herba-alba* (Daudi *et al.,* 2023).

The HOMO and LUMO of the contact determine its capacity to send and receive electrons, respectively. As shown in **Figure 10**, the electron densities of HOMO for the cellulose inhibitor forms are mainly in the 6-(hydroxymethyl)-2-methoxy-5-methyltetrahydro-2H-pyran-3,4-diol regions bound to oxygen heteroatoms and -OH groups. These sites could donate electrons to the surface of the steel to form coordinate bonds, whereas the electron densities of LUMO mainly focus on the other side on 6-(hydroxymethyl)-5-methoxy-2-methyltetrahydro-2H-pyran-3,4-diol regions bound to oxygen heteroatoms and -OH groups, which means that these atomic centers could be the steel electron acceptor to form bonds. Cellulose inhibitor reactive sites were verified by the MEP study. MEP is a visual method for understanding electrophilic and nucleophilic attack sites (Dagdag *et al.,* 2022). Nucleophilic and electrophilic centers are shown by a negative (red) and positive (blue) potential, respectively. As shown in **Figure 10**, the red region is distributed over the oxygen sites, which means that these sites are the active centers that contribute to the formation of covalent bonds with a MS surface (Daudi *et al.,* 2023).

Monte Carlo (MC) and Molecular dynamics (MD) Simulations study

Study of Daoudi et al. (Daoudi *et al.*, 2023) indicates both significant interacting systems and the structural analysis of molecules can benefit from the use of MC and MD simulations. These simulations act as dynamic and structural models for comprehending experimental data. Using MC as well as MD simulations, the activity of inhibitors upon this surface was investigated. These methods are helpful and cutting-edge tools for researching how inhibitors interact with metal surfaces (Hsissou *et al.,* 2018). The equilibrium configurations of the biopolymer CHA inhibitor molecules are shown in **Figure 11** on the Fe (110) surface.

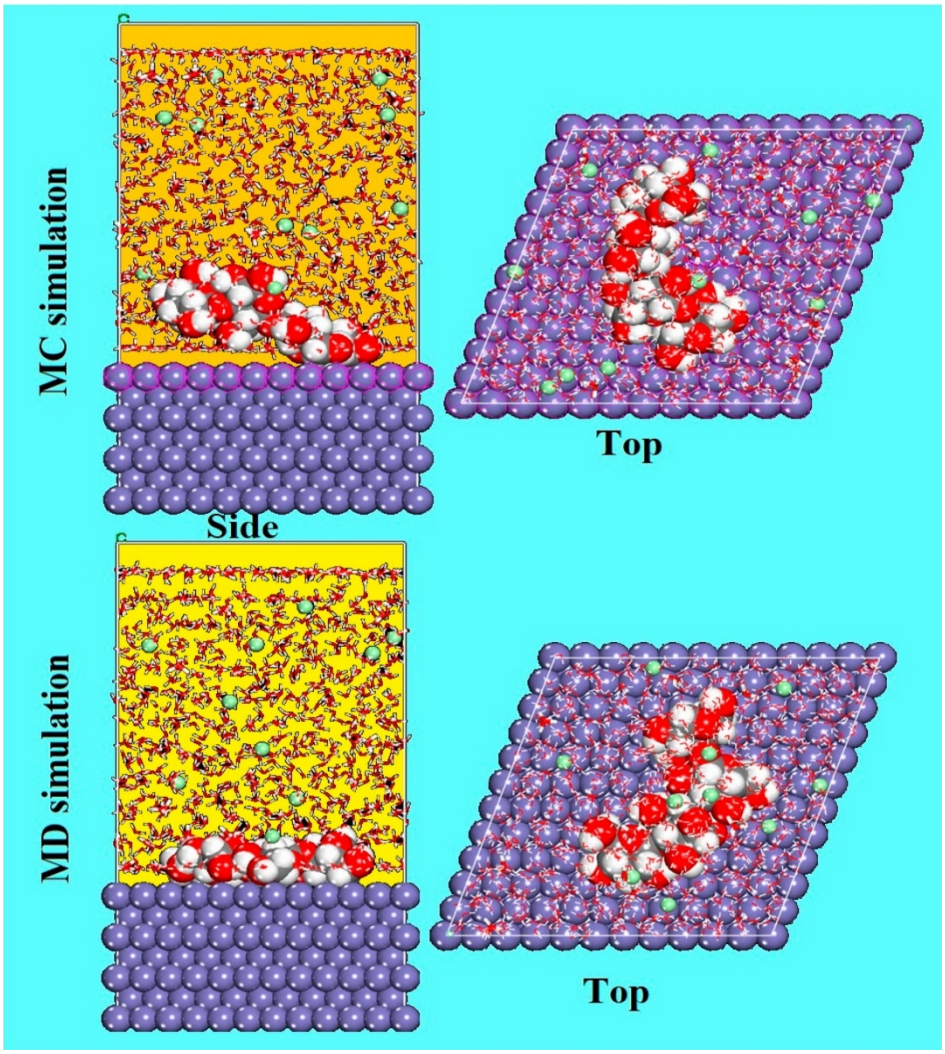

Figure 11. MC and MD simulations results from adsorption configurations and positions of the biopolymer CHA molecule present in the leaves and stems of *Artemisia herba-alba* (Daudi *et al.,* 2023).

The creation of the nearly parallel orientation on the steel surface is due to the relatively similar distribution of HOMO and LUMO concentrations throughout the molecule (the molecule's interaction with the iron atoms). **Figure 12** depicts the computed adsorption energy. The strong connection in-between the inhibitor molecule and the Fe surface, as indicated by the substantial negative value of adsorption energy, reveals the spontaneity of the adsorption process (Berdimurodov *et al.,* 2022b). The cellulose molecule's high E_{ads} value (-295.35 kcal/mol) demonstrates its higher stability (inhibitor/surface contact), which raises the efficacy of its inhibition. This outcome is consistent with the inhibition efficiencies that were established through experimentation. The last few years have seen a rapid increase in the use of MD simulations to under- stand the interaction between the corrosion inhibitor and the metal surface (Haldhar *et al.,* 2021b). Thus, in this study, an MD simulation was performed to study the adsorption behavior of the cellulose inhibitor on an Fe (110) surface. The most energetic stable positions of cellulose inhibitors are found by studying the temperature variations in MD simulation analyses.
As seen in **Figure 13**, the temperature drift is minimal, suggesting that the MD of our system was effective (El Faydy *et al.,* 2021). The iron-atom bond length with the biopolymer CHA molecules found in *Artemisia herba-leaves alba*'s and stems was measured using RDF analysis. Calculating bond length values allowed us to identify the various sorts of bonds that were produced

(Berdimurodov *et al.,* 2022b). The sort of adsorption events resulting on the metal is indicated by peaks in the RDF graph that appear at certain distances from the metal surface (Dagdag *et al.,* 2020). The chemisorption process is considered whenever the peak is present within 1 Å and 3.5 Å; however, for physisorption, the RDF peaks are anticipated to be present at distances larger than 3.5 Å. Because of the closeness of the biopolymer CHA molecule present in the leaves and stems of *Artemisia herba-alba* atoms to the metal surface, as shown in **Figure 13**, the derived cellulose molecules have a relatively strong interaction with the surface. This association is what supports the reflected inhibitory performance of the inhibitor (Molhi *et al.,* 2021).

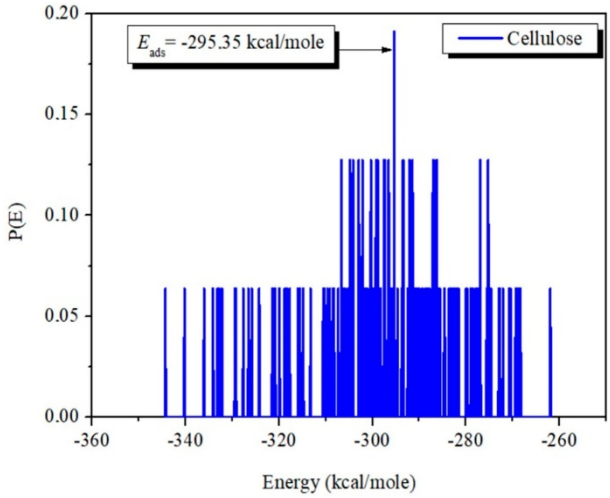

Figure 12. Distribution of the E_{ads} of the biopolymer CHA inhibitor via MC simulation (Daudi *et al.,* 2023).

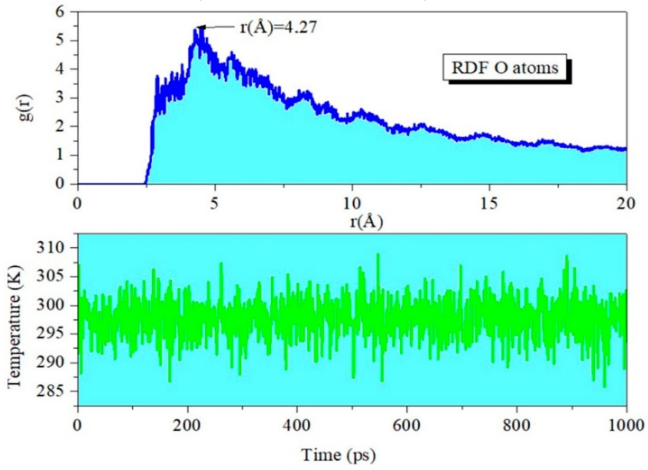

Figure 13. The temperature variation (T = 298 K) and the RDF of the O atoms for the biopolymer CHA molecule found in *Artemisia herba-alba* stems and leaves (Daudi *et al.,* 2023).

Chemical composition of Artemisia herba-alba essential oil

Various studies relating to the chemical composition of essential oils of the species Artemisia herba alba have been described (Salido *et al.,* 2004), (Haouari and Ferchichi, 2009). This work highlights a great chemical variability. For example, a study concerning the chemical composition for samples of essential oils originating in **Spain** (several harvesting sites): revealed the existence of several chemotypes: An essential oil rich in p-cymene (19.9%), it also contains α-pinene (17.2%), myrcene (10.9%), 1,8-cineole (8.6%) and camphor (8.5%). A second chemotype characterized by the predominance of cis-chrysanthenol (28.8%), it also contains 1,8-cineole, p-cymene, and camphor. Another sample is dominated by 1,8-cineole (18.8%), camphor (10.2%), and p-cymene (6.7%). An

essential oil containing davanone (29.1%), p-cymene (9.2-18.4%), γ terpinene, and myrcene. 1,8-cineole (50%) is the majority product in the sample from the **Palestinian desert**. This sample also contains α and β thujones (27%) and other oxygenated monoterpenes; terpinene 4-ol (3.3%), camphor (3%), and borneol (3%) (Feuerstein *et al.,* 1986). A study shows the richness of the essential oil of A. herba alba from **Jordan** in α, β-thujone (16.2%) and (8.5%) respectively, this essence also contains santolina alcohol (13%), and Artemisia ketone (12.4%). It also contains traces of 1,8-cineole, camphor, and chrysanthenyl acetate (Hudaib and Aburjai, 2006). Another study showed that cis β-terpineol is the major component (11.3%) of the sample from Iran. Camphor, sabinene, and camphene, being present with appreciable contents (16.11, 5.18, 4.8%) (Nezhadali *et al.,* 2008). The essential oil of A. herba alba **Tunisienne** is rich in α-thujone (43-85%), trans-sabinyl acetate (17 46%), and β-thujone (10.10%), it also contains: 1,8-cineole (3.3 %) and chrysanthenone (2.32%) in small quantities. Paolini et al. (Paolini *et al.,* 2010) studied the chemical compositions of 16 samples of essential oil of Artemisia herba alba collected in **Eastern Morocco.** A detailed analysis of essential oils led to the identification of 52 components representing 80.5 to 98.6% of the total oil. The chemical compositions studied showed significant qualitative and quantitative differences. According to their main components (camphor, chrysanthenone and α-and β-thujone), three main groups of essential oils have been found. This study also revealed regional specificity of the main components.

The chemical composition of essential oil was characterized by 27 compounds, which accounted for 95,2% of the total oil. The essential oil was characterized by high amounts of β-thujone 12 (38.9%). The other major components were camphor 14 (5.6%), 1,8-cineole 8 (7.1%) and α-thujone 11 (5.4%). The 22 other compounds are reported in low amounts in this essential oil (Chaouche and Haddad, 2023). The oil was dominated by oxygenated monoterpenes (64.0%) followed by monoterpene hydrocarbons (10.0%). The sesquiterpene hydrocarbons and oxygenated sesquiterpenes accounted only for 3.5% and 6.5% of the total essential oil, respectively. It should be noted that several studies have been published on the chemical composition of Artemisia herba-alba. The main compounds in the essential oil of Artemisia herba-alba from **Algeria** were α-thujone (31.50-41.23%) and camphor (16.20-24.58%) (Segal *et al.,*1987). Dahmani-Hamzaoui and Baaliouamer et al. (Dahmani-Hamzaoui and Baaliouamer, 1987) observed that the main compound found were camphor (49.3%) and 1,8-cineole (13.4%), which are the same main compounds found in this study. In essential oil of Artemisia herba-alba from **Tunisia** α-thujone was observed as the dominant constituent (Bendjilali *et al.,*1982), followed by α-thujone, camphor, chrysanthenone or trans-sabinyl acetate. several studies have been published on the chemical composition of Artemisia herba-alba from **Maroc** (Holeman *et al.,*1991), and showed that the composition of the essential oil was rich in α-thujone (60%). In general, this variation in the chemical composition can be understandable according to exogenous factors: the period of sunshine, the nature and the composition of the ground (Ebenso and Ekpe, 1996). According to Mighri et al. (Mighri *et al.*, 2010) it was reported the existence of some EOs that are dominated by major compounds such as (camphor, α or ß-thujone, chrysanthenone, chrysanthenyl acetate, or davanone), and other EOs that are distinguished with the presence of two or more of these compounds at appreciable levels.

Mechanism of corrosion inhibition by *Artemisia herba-alba*

The effective adsorption of corrosion inhibition requires the presence of multiple bonds and the heterocyclic compounds having heteroatoms such as nitrogen, sulfur, oxygen, phosphorus, etc. (Dagdag *et al.,* 2019b), (Benhiba *et al.* 2020), (Hsissou and El Harfi, 2018), (Hsissou *et al.,* 2020), (Saxena *et al.,* 2020). The existing results show that the organic inhibitors adsorbed on the metal surface, either

by physical or chemical adsorption, or simultaneously, possibly form a protective layer (Boudalia *et al.,* 2019), (Ambrish *et al.,* 2019), (Chakravarthy *et al.,* 2014), (Caroline *et al.,* 2015).
AHAEO contains several organic compounds of high molecular weight with heteroatom in their chemical structures. The organic compounds have functional groups such as –OR, –C=O, and aromatic ring, which can adsorb on Al surface through nonbonding electron pairs from oxygen atoms as well as π-electrons present in (C=C) double bound, thus reducing the surface area that is available for the attack of the acid solution. However, synergistic effects may play an important role on the inhibition efficiency of AHAEO as an inhibitor. Camphor, the one major component, is known for its good corrosion I.E. in acid solutions (Hechiche *et al.,* 2019), (Bourazmi *et al.,* 2018). Daoudi et al. (Daoudi *et al.*, 2023) studied the inhibitive effect of *Artemisia herba alba* on the corrosion of MS in 1 M HCl. In this study, it is widely assumed that inhibitor adsorption on the metal–solution interface is the initial step in the corrosion inhibition process in an aggressive acid solution. Molecular structures of the major constituents of the AHAEO are shown in **Figure 14.** The intermolecular synergistic effect of the various components is the widely accepted interpretation of several authors to explain the action of natural extracts on corrosion inhibitors (Andreani *et al.*, 2016), (Aouniti *et al.*, 2022), (Lrhoul *et al.*, 2023), (Sanjay *et al.*, 2024).

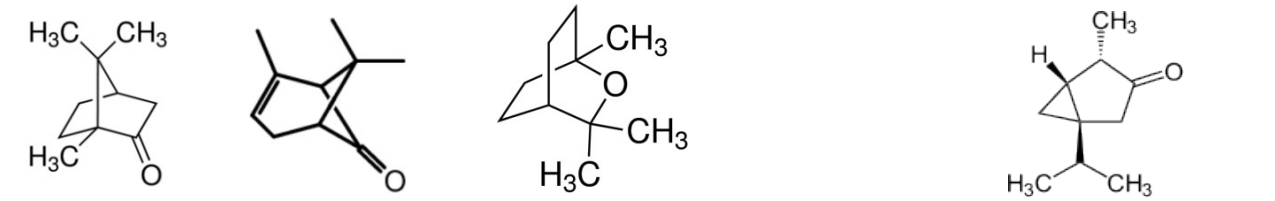

Figure 14. Molecular structure of the major constituents of the AHAEO (Hechiche *et al.,* 2019).

The following mechanism is hypothesized for the interaction of inhibitors on the surface of MS in an acid solution (Heydari *et al.,* 2018), (Ganjoo *et al.,* 2022). The uncharged inhibitor molecules can then interact chemically with the metal surface. The presence of heteroatoms (O) in the inhibitor molecule with unbound lone pair electrons may facilitate chemical adsorption of the inhibitor on the metal surface (**Figure 15**) (Ouass *et al.,* 2021).

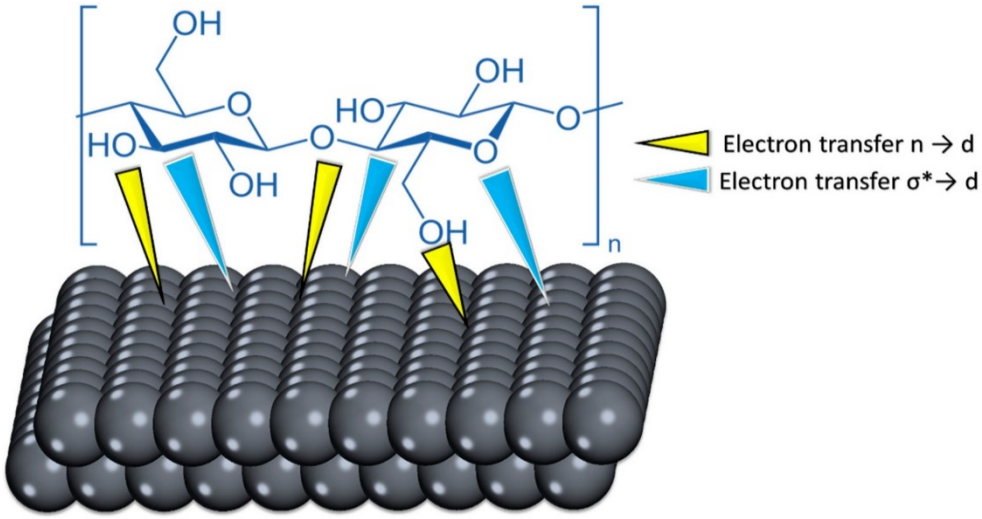

Figure 15. Schematic illustration of the adsorption mechanism of the biopolymer CHA onto MS (Daudi *et al.,* 2023).

Conclusion

In this review, various research works on the corrosion inhibition of different metals and alloys in different acidic media by *Artemisia herba-alba* as green inhibitor were presented. Langmuir, Frumkin and Temkin adsorption isotherms were observed. *Artemisia herba-alba* extract behaved as a cathodic or mixed-type of inhibitor. The maximum inhibition efficiency for *Artemisia herba-alba* was found to be 95.85 % (WL data) and 96.98 (PDP data). The results obtained from weight loss data were in good agreement with the results obtained from the PDP and EIS methods. Various techniques such as SEM, FT-IR, GC-MS, DFT, UV-Vis. etc. were used to study the corrosion mechanism.

Disclosure statement: *Conflict of Interest:* The authors declare that there are no conflicts of interest.
Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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