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Valorization of essential oil and extracts of *Artemisia herba alba* in the inhibition of corrosion and antibacterial and other effects- Review

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Abstract

The use of inhibitors for slowing the corrosion of metals and alloys which are in contact with an aggressive environment is a common practice. A large number of synthetic organic compounds have been studied and are being studied to study their potential for inhibiting corrosion. All these studies reveal that organic compounds, in particular those with N, S and O, have shown significant inhibition efficiency. But, unfortunately, most of these compounds are not only expensive but also toxic to living things. Needless to point out the importance of cheap and safe corrosion inhibitors. Essential oils and aromatic and medicinal plant extracts have become important as an environmentally friendly, readily available and renewable source for a wide range inhibitors. These are the rich sources of ingredients that have a very high inhibition efficiency. Also, the plant world offers an almost inexhaustible source of active ingredients that are essential oils, capable of relieving small everyday ailments and more serious pathologie. Essential oils are used in a wide variety of fields. Scientific data on fundamental aspects obtained by the study of plants, in particular their EO, make it possible to propose actions for their valuation in various fields: pharmacological, perfumery, cosmetics, food industry. This article gives a living overview of the use of *Artemisia herba alba,* Photo1, a natural product used as a corrosion inhibitor for various metals and alloys in aggressive environments.

Keywords: Artemisia herba alba, green inhibitor, metals, natural plant

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Photo 1 : *Artemisia herba alba*

1. Introduction

Pure metals and alloys react chemically and electrochemically with a corrosive medium to form a stable compound, in which loss of metal occurs. The compound thus formed is called corrosion product and the metal surface corrodes. Corrosion involves the movement of metal ions in the solution at the active areas, in this case the anode, the passage of electrons from the metal to an acceptor with less active areas, the cathode. An ion current in the solution and an electronic current in the metal. The cathodic process requires the presence of an electron acceptor such as oxygen or oxidizing agents or hydrogen ions [1–9]. Corrosion can be minimized by appropriate strategies which in turn delay or completely stop the anodic or cathodic reactions or both.

Among the various methods of corrosion control and prevention, the use of corrosion inhibitors [10–16] is widely used. Corrosion inhibitors are substances which, when added in small concentrations to corrosive media, reduce or prevent the reaction of the metal with corrosive media. Inhibitors are added to many systems, namely cooling systems, refinery units, chemicals, oil and gas production units, boiler, etc. Inhibitors work by adsorption of ions or molecules on the metal surface. They reduce the corrosion rate by the following aspects:

The increase or decrease in the anodic and / or cathodic reaction.

The decrease in the diffusion rate of reagents on the surface of the metal.

The decrease in the electrical resistance of the metal surface.

Inhibitors are often easy to apply and offer the advantage of application in situ without significantly disrupting the process. However, several considerations must

Enter the choice of an inhibitor:

The cost of the inhibitor can sometimes be very high when the equipment involved is expensive or when the quantity required is large.

The toxicity of the inhibitor can cause adverse effects on humans and other living species.

The cost of the inhibitor and its availability, And finally respect for the environment.

Authors [17] provide a review of organic corrosion inhibitors, including classification and mechanism of action. They attributed the inhibition of corrosion to the donation of a single pair of electrons to metal atoms. A number of heterocyclic compounds [18–21] have been reported as corrosion inhibitors and screening for synthetic heterocyclic compounds continues. Although many synthetic compounds have shown good anti-corrosion activity, most of them are highly toxic to humans and the environment. The safety and environmental issues of corrosion inhibitors that have appeared in industries have always been a concern. These inhibitors can cause reversible (temporary) effects or irreversible (permanent) damage to the organ system, namely the kidneys or liver, or to disrupt a biochemical process or to disrupt a system enzyme in a place in the body. Toxicity can manifest itself either during the synthesis of the compound or during its applications. These toxic effects have led to the use of natural products as environmentally friendly and harmless anticorrosion agents. In recent days, many alternative ecological corrosion inhibitors have been developed, they come from rare earth elements [22–24] with organic compounds [25–28]. A medicinal plant is a plant that is cultivated or gathered in its natural environment for its medicinal properties [29]. Humans have used plants for thousands of years to treat various ailments. The plant world is the source of a large number of medicines. Recently, researchers have estimated that there are around 400,000 species of plants in the world, of which about a quarter or a third have been used by companies for medicinal purposes [30]. In several developing countries, a large part of the population trusts traditional medicine and herbalists and their collections of medicinal plants for healing. In this review, a detailed account of green inhibitors is given in this case white *Artemisia herba alba.*

2.Composition of essential oils and aromas:

Today, 300 of 3000 essential oils are commercially important. Aromatic plants produce enough of it. The plants considered rich in EO most often belong to the Lamiaceae family (oregano, lavender, thyme, sage, mint etc.), Apiaceae (anise, cumin, caraway etc.), Myrtaceae (eucalyptus, niaouli etc.) , Pinaceae (pine, cedar, etc.), Rutaceae (lemon, orange), and Lauraceae (cinnamon, camphor tree, etc.) [31]. The chemical composition of an essential oil can vary within the same botanical genus, these variations can be observed within the same species. It actually depends on various extrinsic parameters (soil, environment, climate), intrinsic (degree of maturity, genetic factors, location), technological (type of crop, method of harvest), as well as the extraction methods. Essential oils and aromas are derived from the secondary metabolism of the plant and can be stored in various structures such as epidermal cells, internal secretory cells, secretory hairs or trichomes [32]. They are complex mixtures of volatile substances made up of about 20 to 60 compounds at different concentrations. Terpenes and terpenoids as well as low molecular weight aromatic components are the major compounds [33].

2.1. Terpenes and terpenoids:

Terpene compounds are widely found in essential oils [34]. Although they have very diverse structures, they are all formed by the joining of isoprenic units ($C5H6$). We thus distinguish according to the number of carbon constituting the molecules of this group: hemiterpenes (1 unit: C5), monoterpenes (2 units: C10), sesquiterpenes (3 units: C15), diterpenes (4 units: C20) , sesterpenes (5 units: C25), triterpenes (6 units: C30), tetraterpenes (8 units: C40) and polyisoprenes (n units: C5n). The most common terpenes found in essential oils are the more volatile terpenes with not too high molecular weight such as mono (C10) and sesquiterpenes (C15) [35]. (C10) alone constitute about 90% of essential oils [33]. Oxygenated derivatives of terpenes called terpenoids. A wide variety of structures characterize terpenoids according to the number of carbons present, the saturated or unsaturated nature of the bonds, the spatial configuration (shape of chair, boat, etc.) and the nature of the functional group. They consist of different functions: [33] (Figure 1).

Phenol: C6H5-OH (thymol),

Alcohol: R-OH (menthol),

Aldehyde: R-COH (citronellal),

Ketone: R1-CO-R2 (carvone),

Ester: R1-COO-R2 (linalyl acetate),

Ether: R1-O-R2 (eucalyptol),

Peroxide: R1-O-O-R2 (ascaridol).

2.2. Aromatic compounds:

The aromatic compounds of essential oils are mainly derivatives of C6-C3 phenylpropane. They are much less common than terpenes. They can include phenols (chavicol, eugenol), aldehydes (cinnamaldehyde), alcohols (cinnamic alcohol), methoxy (anethol, estragol) or methylene dioxy (myristicin, safrole) derivatives [32]. The structure of the different molecules is shown in Figure 2.

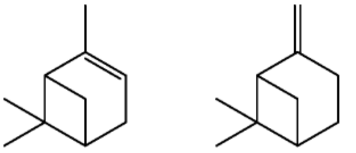
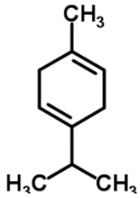
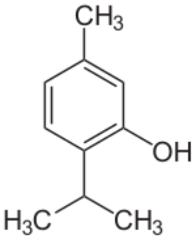
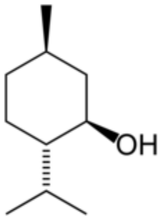
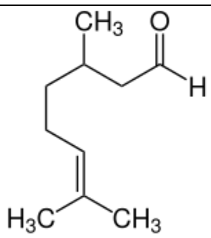
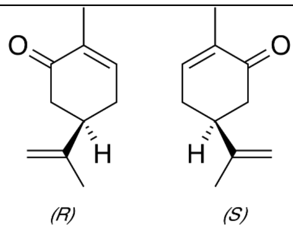
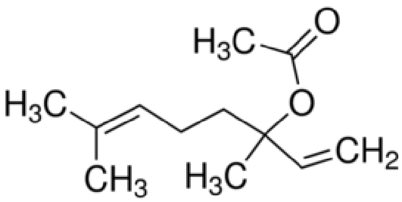
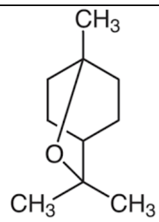
 pinene	 ϒ-terpinene
 thymol	 (1R, 2S, 5R) menthol
 citronellal	 carvone
 Linalyl acetayte	 eucalyptol (1,8-cineol)

Figure 1: structure of the different compounds of terpenes and terpenoids.

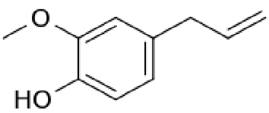
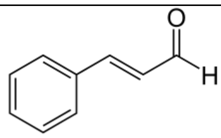
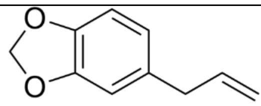
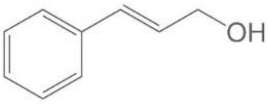
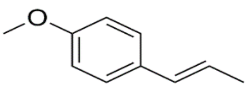
 eugenol	 cinnamaldehyde	 safrole
 Alcool cinnamique	 anethole	

Figure 2: Aromatic structure of terpenes and terpenoids

Nitrogenous or sulfur compounds such as glucosinolates or isothiocyanate derivatives are also characteristic of secondary metabolites of various plants. For example, sulfur compounds are predominantly present in the essential oils of plants of the Alliaceae family [37].

Known for millennia, white sagebrush was described by the Greek historian Xenophon at the beginning of the fourteenth century BC, in the steppes of Mesopotamia [38]. It was then listed in 1779 by the Spanish botanist Ignacio Claudio de Asso y del Rio [39]. It is an essentially fodder plant, much appreciated by cattle, it has a characteristic odor of thymol oil and a bitter taste hence its astringent character [40]. Artemisia herba alba is a spontaneous plant widely distributed in North Africa and the Middle East, it prefers dry and hot climates, and exists in the form of large populations in desert areas [41]. It is a steppe plant from the Iranian-Turanian regions, predominant in the steppes of Spain as well as in the Sinai desert [42].

In Morocco, / '*Artemisia herba* alba occurs spontaneously, white sagebrush reigns in a quasi-desert landscape [43]. In Algeria, *Artemisia herba alba*, covers nearly six million hectares in the steppes, it appears in the form of white, woolly and spaced bushes [44].

In traditional pharmacopoeia, white *artemisia herba alba* has long been known by pastoral and nomadic populations for its laxative properties. It is used in particular as an anthelmintic in sheep. Freidman and cool. (1986) [38], reported that the infusion of white mugwort is used enough by the Bedouin of the Negev (Israel) to relieve gastrointestinal ailments [45].

In Iraq, it is prepared with tea and is one of the forms of self-medication for non-insulin-dependent diabetes (DNID) [46].

2-3- Chemical composition of the essential oil

Various studies relating to the chemical composition of essential oils of the species *Artemisia herba alba* have been described [47,48]. 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%) [49].

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 [50].

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%) [51]. 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.

J. Paolini et al [52] 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.

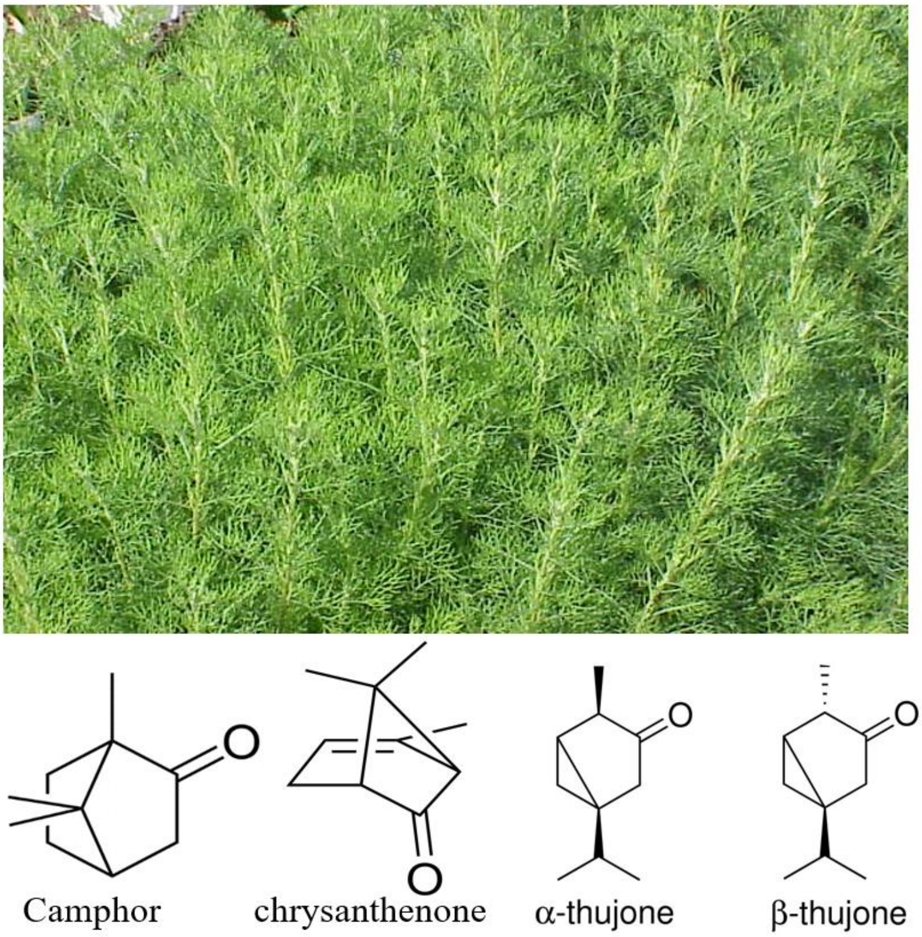


Figure 3: Major compounds of *Artemisia herba-alba* collected in eastern Morocco

2-4-Study of antibacterial activity

In the present study, a team [53], studying the antibacterial activity in vitro against various bacterial strains and the chemical composition of the essential oil of *Artemisia herba-alba* were studied. Acute toxicity by determination of the median lethal dose was also studied. The results of the gas chromatography / mass spectrometry analysis of the the essential oil gave 19 compounds representing 98.7% and the main constituent was camphor with an amount by 50.7%. A significant antibacterial effect was observed against Klebsiella oxytoca (31.3 mm) and against Acinetobacter baumannnii (47.6 mm). The results of this study suggest that the essential oil of Artemisia herba-alba may be a source of natural antibacterial agents with potential pharmacological applications.

Fekih *et al.* [54], have tested the antibacterial effects of three essential oils were tested against three bacterial strains (ATCC: Staphylococcus aureus, Escherichia coli and Pseudomonas aeruginosa) commonly known for their implication on healing infections. The evaluation of essential oils in combination revealed that the the maximum concentration required was 0.5 ml / ml for *Artemisia herba alba*. Therefore, various studies [55-60], were conducted toto assess the potential of *Artemisia herba alba* as a source of health-promoting constituents. Besides, the antioxidant, the antimicrobial and the cytotoxic potentials were evaluated. A total of 86 metabolites, including C-glycosylated and methylated flavones, quinic acid derivatives, coumarins, sesquiterpenes lactones, terpenoids, fatty acids, carbohydrates, organic acids and alkaloids were identified, sixty-five of them were reported for the first time in A. herba alba. The proliferation and growth of solid tumor cells in mice with solid Ehrlich carcinoma tests indicated that oral administration of extract of *A. Herba alba* resulted in significant reductions in tumor size. Thus, we concluded that the extract of *A. Herba alba* showed promising potential anti-tumor efficacy with greater safety than artesunate and the anticancer drug cisplatin used commercially in mice. Abu-Darwish *et al.* [56] concluded that it was possible to find appropriate doses of *A. herba-alba* oil with both antifungal and anti-inflammatory activities and without detrimental effects towards several mammalian cell types. These findings add significant information to the pharmacological activity of *A. herba-alba* essential oil, specifically to its antifungal and anti-inflammatory therapeutic value, thus justifying and reinforcing the use of this plant in traditional medicine.

2-5- Natural corrosion inhibitors

In 2002, Ouachikh et al [61] use the essential oil of *Artemisia herba alba* (Art) as a steel corrosion inhibitor in 0.5 M H_2SO_4 using weight loss measurements and electrochemical polarization methods. The results collected show that this natural oil reduced the rate of corrosion. Hammouti et al. are studying, *artemisia* oil [62,63] for corrosion inhibition of steel in medium acid. Authors [64], use the essential oil of *Artemisia herba-alba* from Morocco which has been hydrodistilled and its chemical composition has been studied by capillary GC and GC / MS. The main components were 1,8-cineole (35.6%) and camphor (24.1%). The results obtained showed that the essential oil of Artemisia reduces the corrosion rate. The Tafel polarization method indicates that the plant extract behaves as a mixed type inhibitor.

Green inhibitors are an important way to reduce the corrosion rate of different metals. Boumhara *et al.* [65] study the corrosion behavior of mild steel (MS) medium in 1 M HCl by aqueous extract of *Artemisia* (AMEO), which is a durable green inhibitor to reduce its corrosive action. by techniques and methods namely: weight loss, electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP), SEM-EDX, XPS and theoretical calculations for the majority molecule. The natural oil acted as an efficient inhibitor against the carbon steel corrosion in 1 M HCl, and its inhibition efficiency increased with the inhibitor concentration reaching a value of up to 92% at 3 g/L. Polarization studies showed that the AMEO was a mixed-type inhibitor. Adsorption of AMEO on the steel surface in 1 M HCl solution followed Langmuir's isotherm and the thermodynamic parameters were determined and discussed. The XPS studies showed that the inhibitive layer is composed of an iron oxide/hydroxide mixture where AMEO molecules are incorporated.

Boumhara *et al.* [66], discuss in detail the mechanisms of adsorption inhibition and the efficiency of various groups (organic and inorganic) of green corrosion inhibitors for steels in aggressive acidic environments, in particular hydrochloric acid (HCl) and sulfuric acids (H_2SO_4). The main components of Artemisia Mesatlantica were β-thujone (33.9%) followed by camphor (7.5%), 1,8-cineole (6.9%) and α-thujone (5.5%). Artemisia Mesatlantica essential oil (AMEO) was tested as corrosion inhibitor of mild steel in 1 M HCl using weight loss measurements. The obtained results showed that inhibition efficiency increases with increasing inhibitor concentration to attain 91 % at 2.76 g/L of AMEO at 303 K. Physical adsorption is proposed for the corrosion inhibition mechanism and the process followed the kinetic/thermodynamic model of El-Awady et al. in the temperature range from 303 to 343 K. The adsorption and kinetic parameters for mild steel/AMEO/1 M HCl system were calculated from experimental gravimetric data and the interpretation of the results are given

Other authors [67-69], study plant biomaterials as inexpensive, non-toxic and biodegradable materials that are found in abundance in nature. They contain heteroatoms and / or pi electrons which make them candidates for the corrosion inhibitor of metals. In recent years, much research has been undertaken on plant biomaterials as corrosion inhibitors of metals in various corrosive media. The corrosion inhibiting activity in many of these extracts could be due to the presence of heterocyclic constituents like alkaloids, flavonoids, etc., even the presence of tannins, cellulose and polycyclic compounds normally enhance formation a film on the metal surface, thus promoting the fight against corrosion.

Conclusion

The recent trend to point out plant extracts as corrosion inhibitors has one main flaw. Numerous studies have been carried out on the identification of the constituent compounds of the extracts and efforts are not always made to specify the active ingredient present.

It is certain that effective natural corrosion inhibitors will emerge in the coming years due to their biodegradability, availability and non-toxic nature. A careful reading of the literature clearly reveals that the era of green inhibitors has already begun.

Artemisia herba-alba collected in eastern Morocco as well as others of the rest of world were largely characterized by various techniques to determine the molecular structures of oil and extract and to serve in medicinal uses

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