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Research Article

Study of Antibacterial Activity, Phytochemicals and Physico-chemical for Green Corrosion Inhibitors in Different Corrosive Media from *Marrubium vulgare* L Crude Extract

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Abstract

The aim of this research study use the *Marrubium vulgare* L. water- ethanolic extract for the inhibition of the corrosion of metals (Iron, Copper and Aluminium) in aqueous solutions, including phytochemicals- physicochemical analysis and antibacterial activity. Which reveled to resulted that this extract as a good inhibitor for selected metals corrosion, also is positively toward existing of phytochemicals which qualitatively analyzed such as alkaloids, flavonoids, tannins and saponins, while, Physico-chemical parameters, quantitatively phytochemical analyzed for obtained alkaloids, flavonoids and saponins were 56.86, 67.35 and 71.83%, respectively. Also, the physico-chemical parameters moisture content, loss on drying, Total Ash value, water-soluble ash, acid-insoluble ash and alcohol-soluble extractive were 11.26, 19.10, 13.40, 7.90, 10.48 and 8.31%, respectively. Furthermore, the volume of H2 of hydrogen producing from the reaction of metal coupons in acidic and alkali medium in were 170, 140, 150, 180, 80 and 40 g/cm3, respectively. And whereas, values varied widely among samples, but in general, most samples were had a good results, and the inhibition was found increased within increasing the concentration of the plant crude extract in solutions medium leads to highest protection of metals from corrosion. As an obtained results, that the crude extract of extract of *Marrubium vulgare* L acts as a mixed-type inhibitor and may aid as an active corrosion inhibitor of metals in aqueous solution. From the acquired results of antibacterial the examination exhibited that the crude extract of leaves was very effective against all types of bacteria *Escherichia Coli, Klebsiella pneumonia, Proteus vulgaris* and *Staphylococcus aureus*. The abstract should be clear, relative, descriptive, self-explanatory and no longer than 400 words. Do not include references or formulae or any special character in the abstract.

Keywords: *Marrubium vulgare* L.; Green Corrosion Inhibitors; Phytochemical and Physicochemical Screening; Antibacterial Activity

Introduction

Phytochemical: Chemical compounds naturally present in the plants have positive or negative health effects, where named as phytochemicals which means by Greek phyton and means plant [1]. There is a large assortment of remedying that could be developed from conventional medications which are necessary for caring and to treat several diseases and healing from it. The Marrubium genus is known as horehound and belongs to the *Lamiaceae* family and grows in warm areas of Northern Africa, Europe and Asia [2]. In Libya *Marrubium vulgare* L., plant known as "Robia" and traditionally used as a folk medicine in different diseases, such as an herbaceous medicine for chronic coughs and colds a sedative agent or pain reliever, asthma, pulmonary infections, hypotension, inflammation and as cholagogues [3]. *Marrubium vulgare* L., generally, used for prevention and the treatment of various ailments as an herbal remedy by folk people as a traditional medicine in Libya, because of including a highly active haling ingredients components, as well as trace metals and minerals. With the developing importance of the remedial benefits from the medicinal plants, the protection and safety-catch from using medicinal plants will increase. Phytoremediation is the advantage of medicinal plants to decrease the concentrations of poisonous influences of pollutions in the humans and environment. The purpose of the physicochemical parameter is essential in the knowledge of contamination and inappropriate method of medications. And more are considered of the model to investigate the integrity and pureness of raw medicines particularly in the medicine formula, including for especially reaching a correct control of pharmaceutical toward drugs quality. Benefits of extractive value are for the estimation of a raw drug material because that provides thought concerning the type of chemical ingredients existing in it and is helpful for evaluation of chemical components, a solvent in that appropriate solution utilised for extraction. The inhibitor is a substance that is added in a small amount to an electrolyte solution to reduce the rate of corrosion of a metal. The inhibitors may be organic or inorganic substances. But it must be able to dissolve into the corrosive medium. Moreover, it must be able to form a protective layer. For example, magnesium and calcium salts are cathode inhibitors. Anodic retarders are used to prevent corrosion in radiators, steams, boilers, and other containers. Corrosion inhibitors reduce the rates of partial reaction or both (anodic oxidation and/or cathodic reduction). Applicability depends on their chemical nature (organic or organic matter), their properties (oxidizing or non-oxidizing compounds), or their technological field of application (pickling, descaling, acid cleaning, cooling water systems, etc.). Chelating agents are organic molecules containing at least two functional polar groups that are able to form coordinate bonds with mineral cations. Both the alkali groups (-NH2 or heterocyclic nitrogen) and the acidic groups (-COOH or SH-) participate in the reaction of the chelation reaction. As a result of this reaction, stable circular structures are created. The most stable structures consist of five-membered rings that contain a metallic ion. Organic corrosion inhibitors containing more than one functional group may act by chelating the metal ion while it is still bound to its crystal system; the metal ion is not dissolved, and the surface chelate acts as a corrosion inhibitor. Surface-active chelating agents act as effective corrosion inhibitors when insoluble surfactants are formed. In contrast, the formation of soluble chelates may stimulate an erosion attack. Different mechanisms of action of chelating agents can be suggested as inhibitors. In some cases, the thickness and physical properties of the surface layer formed in solutions inhibited by chelating agents may support the surface chelating reaction formed between the organic additive and the dissolved metal ion. The thick layer forms a physical barrier, which impedes the contact between the electrolyte and the metal surface.

Aim of the Study

The aim of this research is to introduce the *Marrubium vulgare* L. plant and which is one of the plant's growth in the Mediterranean countries, it grows in the coastal areas of the city of Khums, and its importance extends from used as a treatment of several diseases in past and nowadays, also to evaluate its microbial activities, and as well as to identify its chemical components and try to use it as a green inhibitor against corrosion of some metals such as aluminum, iron and copper.

Materials and Methods

Collection of plant material

The plant sample of *Marrubium vulgare* L. was collected from Alkhums district. It was authenticated by Department of Biology,

Plant Division Faculty of Sciences El-Mergib University Alkhums Libya. The fresh leaves of plant sample were separated rinsed with tap water and then with deionized water. It was dried, cut, crushed and pulverised with the help of an electric blender and then the soft dried powder sample was stored in dark bottles until further processes.

Extraction

40g of the soft dried powdered leaves of *Marrubium vulgare* L. were extracted with 400 ml of water: ethanol (1:1) by maceration for 72 h., at room temperature and then solvent, was removed at 40°C using a rotary evaporator. Finally, a brown greenish extract weighing 85% was obtained and kept in an airtight dark bottle in a refrigerator for further study.

$$\textit{Extraction Yield (\%)} = \frac{\textit{Mass of extracted product}}{\textit{Mass of raw material}} \; X \; 100 \qquad (1)$$

Phytochemical screening (Qualitative determination)

Preliminary phytochemical screening of the crude extract to identify the chemical constituents of this plant procedures were carried out according to standard methods employed to examine for the presence of tannins, saponins, flavonoids, alkaloids [4-7].

Determination of alkaloids

2g of the water alcoholic extract was mixed with 6 ml of 2N HCl then was heated on a boiling water bath. After that cooled, filtered and the filtrate was divided into two equal portions:

- **Hager's test:** First portion is treated with Hager's reagent (saturated picric acid solution). Formation of yellow colored precipitate indicates the presence of alkaloids.
- **Wagner's test:** Second portion is treated with Wagner's reagent (iodine in potassium iodide). Formation of brown/reddish precipitate indicates the presence of alkaloids.

Detection of flavonoids

Ammonia test

- The fumigated of crude extract solution by ammonia on a silica gel plate, if a yellow or yellow fluorescence under UV light appeared, indicates the presence of flavonoids.
- 2 ml of the crude extract was treated with a few drops of ammonia then was observed under UV and visible lights lamp; the observing of fluorescence indicates the presence of flavonoids.

Aluminum chloride test

One drop of the crude extract solution was placed on a filter paper then dried it after that was sprayed with some aluminums chloride reagent. If the yellow spot or yellow-green fluorescence appears under ultraviolet light, it indicates the presence of flavonoids.

Detection of tannins

- **Mitchell's test:** A few amounts of ammonium ferric citrate crystals were added to the crude extract, which gives a clear soluble solution, then a solution of ammonium acetate was added to it, will forming of an insoluble solution of iron-tannin complex (suspension).
- **Vanillin hydrochloric acid test:** To the crude extract solution 3 - 4 drops of vanillin-hydrochloric acid reagent is added, the appearance of red colour indicates the presence of tannins.

Detection of saponins

- **Froth test:** 10 mL of distilled water was added to the crude extract, then vigorously shaken for 3 minutes then divided into two portions:
  - **First portion:** The first portion was allowed to stand for 10 min. If stable froth appears, it indicates the presence of saponins.

- **Second portion:** To the second portion was added 3 drops of olive oil and agitated vigorously for a stable persistent froth. The formation of emulsion indicated the presence of saponins.

Phytochemical screening: (Quantitative determination)

Determination of total alkaloids

3g of the grounded leaves samples were mixed with 50 ml of 10% acetic acid in ethanol solution in a covered conical flask and left aside for 4h. After that, it was concentrated to one-quarter from its volume on a water bath. To this extract, concentrated ammonium hydroxide was added by dropwise until the precipitation was achieved. The complete solution was allowed to settle and the precipitate was obtained and washed with dilute ammonium hydroxide and then filtered. The residue is the alkaloid, which was dried and weighed [8]:

$$\text{Alkaloids Extraction Yield (\%)} = \frac{\text{Mass of extracted product}}{\text{Mass of raw material}} \; X \; 100 \qquad (2)$$

Determination of total flavonoids

3g of the grounded leaves sample were mixed with 15 ml of 80% aqueous methanol at room temperature. The complete solution was filtered through Whatman filter paper No 42 (125 mm) into a weighed beaker and for evaporating to become dryness transported to a water bath until a constant weight was obtained [9].

$$\text{Flavonoids Extraction Yield (\%)} = \frac{\text{Mass of extracted product}}{\text{Mass of raw material}} \; X \; 100 \qquad (3)$$

Determination of total saponins

4g of the grounded leaves samples were mixed with 20 ml of 20% aqueous ethanol solution in a conical flask. And then placed in a water bath and heated for 4h., with stirring at about 55°C. The mixture was filtered and the residue re-extracted with another 40 ml of 20% ethanol. The combined extracts were concentrated over a water bath at nearly 90°C. The concentrate was transferred into a 250 ml separating funnel and 20ml of diethyl ether was added and shaken strongly. The aqueous layer was collected while the ether layer was discarded. The purification manner was repeated. 20 ml of n-butanol was added. The combined n-butanol extracts were washed twice with 5 ml of 5% aqueous sodium chloride. The residual solution was warmed in a water bath. After evaporation the sample was dried in the oven to constant weight; the saponins content was calculated [10]:

$$\text{Saponins Extraction Yield (\%)} = \frac{\text{Mass of extracted product}}{\text{Mass of raw material}} \; X \; 100 \qquad (4)$$

Determination of physico-chemical parameters [11,12]

Determination of pH

PH range was determined by using a standard simple glass electrode pH meter, formulations in 1% w/v which means a 1g; were dissolved in a 100 ml of water-soluble portions of whole plant powder, and pH result as showed in table 1.

Physical evaluation

Solubility

1g of fine powder was placed in each test tube, separately, and the appropriate solvent was added to it (distilled water, ethyl alcohol, ether and chloroform, separately) and the results were reported.

Determination of moisture content

10g of the soft dried powder sample of *Marrubium vulgare* L was set in a moisture dish in an oven at 100 - 105^{0}C and dried to a constant. The loss of weight of the soft dried powder sample was calculated in mg/g.

$$\text{Moisture content (\% w/w)} = \frac{\text{Inetial weight of sample} - \text{Inetial weight of sample}}{\text{Inetial weight of sample}} X\,100 \qquad (5)$$

Determination of loss on drying

1g of the soft dried powder sample of *Marrubium vulgare* L. were placed into weighed petri dish plate and the contents were spread straight to a depth about 10 mm approximately. The weighted plate was heated at 105^{0}C in a hot air oven for 1 hr. and then cooled in desiccators; loss in weight was recorded as moisture content. Respective moisture content percentage of the samples was calculated.

Determination of total ash value

$$\text{Moisture Content (\% w/w)} = \frac{\text{weight of Ash sample}}{\text{Inetial weight of sample}} \; X\,100 \qquad (6)$$

A clean silica crucible was ignited, cooled and weighing and then a 2g of the soft dried powder sample of *Marrubium vulgare* L. were placed in it and burned in a muffle furnace at 505^{0}C for 4 hr., where it was incinerated by gradually increasing in a muffle furnace. The ignition was repeated until achieved of constant weight. Subsequent total ash, it was cooled in a desiccator, then the percentage of the total ash with reference to the soft dried powder sample of *Marrubium vulgare* L, was calculated:

$$\text{Total Ash Value (\% w/w)} = \frac{\text{weight of Ash sample}}{\text{Inetial weight of sample}} X\,100 \quad (7)$$

Water-soluble ash

The total ash was removed from the crucible into 100 ml beaker using 30 ml of chloroform water and it was boiled for 5 min over a Bunsen burner and filtered by ashless filter paper (Whatman No: 42). The residue was washed with warm water, ignited to ash cooled and weighed. The weight of insoluble ingredients was decreased from the weight of the ash. The variation in weight represents the water-soluble ash. The percentage of water-soluble ash was calculated with relating to the soft dried powder sample of *Marrubium vulgare* L:

$$\text{Water soluble ash (\% w/w)} = \frac{\text{ash weight}}{\text{dried powder sample}} X\,100 \quad (8)$$

Determination of acid-insoluble ash

To the total ash crucible, 10 ml 2N of HCL was added and covered then gently boiled for 5 minutes. The acid-insoluble material was collected on an ashless filter paper and washed with hot water till the filtrate was neutral. The ashless filter paper returned to the crucible and ignited to a constant weight, then was allowed to cool in a desiccator and weighed. The content of the acid-insoluble ash of the soft dried powder sample of *Marrubium vulgare* L. was calculated in mg/g:

$$\text{Acid soluble ash (\% w/w)} = \frac{\text{ash weight}}{\text{dried powder sample}} X\,100 \quad (9)$$

Determination of alcohol-soluble extractive

Precisely, 4g of weighed of the soft dried powder sample of *Marrubium vulgare* L. was put in a glass stoppered round bottle flask, and 100 ml of ethyl alcohol was added to the flask and then, it was agitated very well and left for 1h., refluxing to boiled gently for 1h, cooled and filtered. Then a 25 ml of the filtrate was transported to a tarred dish and evaporated to dryness by using a water bath. Then the dish was transferred to the oven for drying at 105°C for 6h, finally cooled in a desiccator and weighed:

$$\text{alcohol-soluble extractive (\% w/w)} = \frac{\text{weight of resedue}}{\text{dried powder sample}} X\,100 \quad (10)$$

Weight loss study

Weight loss studies were conducted at room temperature (g/l at 25 ± 2^{o}C) where it was done by immersing metal pieces (iron, copper and aluminum, each separately) with a thickness of 2 mm and a size of 3 x 3 cm which had been cleaned previously, wherewith polished by sandpaper, washed thoroughly with tap water, after that was done with distilled water, dried with acetone and then precisely weighed. Subsequently, it was placed in a 250 ml beaker so that it was immersed by 100 ml of the prepared solution for immersion (0.5 M Hydrochloric acid solution, 0.5 M Na OH solution, separately) The solutions were in the absence or presence of the plant extract in different concentrations for 24 hours, 48 hours and 72 hours. Metal pieces were then removed, dried with a warm air dryer and as a final point were accurately weighed after every 24 hours the exact time for this. Then the weight loss was calculated and thus the corrosion rates CR, surface coverage (θ) and inhibition efficiency% (EI) was calculated for each piece or coupon used using the following equations:

$$\text{Weight loss (g)} = W_1 - W_2 \quad (1)$$

Where, W1=Initial weight of coupon, W2 = Weight of coupon after treatment.

$$\text{Corrosion Rate (CR) } (g.cm^{-2}h^{-1}) = \frac{W_2 - W_1}{A\,X\,T} \quad (2)$$

Where, W1= initial weight of coupon, W2 = weight of coupon after treatment, A = surface area, T = Time in Hours.

$$\text{Surface coverage}(\eta\%) \quad \frac{CR_B - CR_I}{CR_B} \qquad (3)$$

Where, CR_B and CR_I are the corrosion rates in absence and presence of the inhibitor, respectively.

$$IE\ \% = \frac{C_R - C_{R(I)}}{C_R} X\ 100 \qquad (4)$$

Where: inhibition efficiency (IE %), Corrosion rate (CR) and CR_I are the corrosion rates in presence of the inhibitor.

Measuring the volume of hydrogen gas produced per unit time

Hoffman's device was used to measure hydrogen resulting from the interaction of metal pieces with an acidic medium or basic medium so that the volume of gas resulting from the reaction can be measured by the gas that collects in the reaction flask and thus creates pressure on the oil (Paraffin Oil) located in the Hoffman's tube. Whereas with the production of more gas, the oil is pushed out and thus the resulting reading of the volume of the gas produced can be recorded by a certain period of time (20 seconds to be exact).

The experiment

In the three-neck flask (150 ml capacity) 100 ml of the selected medium for the reaction (acid, basic, solutions separately) in this fixed the metals coupons through the two necks side of the flask into the medium reaction flask, and on the other side of coupons were connected by an electric source. And through the middle neck, a Hofmann's apparatus was attached. The reading is recorded by the rise of the paraffin's oil level in Hofmann's apparatus that results from the pressure of the gas which produced from the reaction in the connected flask. Note that all the tests were conducted at room temperature 25 ± 2°C and at a time of 20 seconds.

Antibacterial Activities

Investigated the crude plant extracts against bacterial growth by a disc diffusion method

The *in vitro* antibacterial activity of crude extract (mixture of ethanolic and water 1:1) of *Marrubium vulgare* L., at 50, 100, 200, 400 and 600 mg/ml was studied by disc diffusion method against each of two gram-negative bacterium *Escherichia Coli, Klebsiella pneumonia, Proteus Vulgaris* and one gram-positive bacterium *Staphylococcus aureus*. Where sterile nutrient agar dishes were prepared and incubated at 37°C for 24h to check for any contamination. Then a sterilized filter paper discs (Whatman No.1) of 6 mm diameter were immersed in five different dilutions of the crude extract and put in a suitable place on the facade of the plate with quadrants designated at the rear of the Petri dishes [36]. The Petri dishes were incubated at 37°C for 24h and the diameter of the zone of inhibition provided in mm. The effect of the crude extract was compared with ciprofloxacin (10 µg/ml). The zone of inhibition was determined by including the minimum dimensions of the zone of no bacterial growth throughout the disc and minimum inhibitory concentrations were prepared. An average of three independent determinations was recorded (Table 17).

Results and Discussion

Due to the remarkable electrical and mechanical properties of metals, they are of great interest on a large scale in the uses of human activities. But because of the chemical reactions between the surface of metals and the environment surrounding them, many products generated throughout these reactions, such as oxides and sulfates, causing damage to it, i.e. corrosion of the metals. Thus, they essential to be protected with natural corrosion inhibitors, and for the effective influence of the natural inhibitors, that is, they have economic benefits and because they are environmentally non-toxic and susceptible to degradation. Also, they are an eco-friendly, ecologically acceptable, and maintainable resource. Consequently, the studied plant's extract's revealed good inhibiting performance to these studied metals (aluminium, iron, and copper) corrosion in used aggressive media. The distinctiveness of some metals with these excellent mechanical properties makes them the most common ones in terms of uses in various industries, for example, mild steel shows high mechanical resistance along with its toughness and durability, which makes it a highly available material and at low cost. Other metals include copper and aluminium, which are no less important than mild steel in uses, and for comparison, copper and aluminium alloys are studied as well. Whereas the high cost correlated with corrosion, and due to the replacement of corroded metals, where it is possible reduced by using corrosion inhibitors that are eco-friendly. For example, the study of the cor-

rosion of metals is a matter of enormous theoretical and practical importance and for that reason has received a great deal of attention. Acidic solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and acidification of oil well, require the use of corrosion inhibitors to limit the corrosion attacks toward metallic materials. Focusing on the use of natural inhibitors and that is from a natural source and that work as anti-corrosion coatings of the metal, particularly in acidic media, is the interest of researchers and scientists increasingly for finding and develop a coating that protects metals from the corrosion process, and this is to avoid the risks of using industrial decomposers from their high costs and toxicity to the environment. Hence, there is a necessity to create advanced brand-new proper coatings for enhanced production, and because most of the industrial inhibitors are poisonous to the environment, the researchers are working to find that green which is eco-friendly corrosion inhibitors. Since Green corrosion inhibitors contain heavy metals or toxic compounds harmful to humans and the environment and also those they are degradable.

Phytochemical screening

The preliminary phytochemical analysis for medicinal plant a vital for the understanding of bioactive practices and which is a unique reference of Curative and manufacturing syntheses that to developing and leads to exploring new formulae.

***Marrubium vulgare* L**	
Extraction Yield (%)	85
pH	6.9

Table 1: The extraction yield and the pH value of *Marrubium vulgare* L.:

Table 1 shows both the pH of the aqueous extract (6.9) and the yield of the cold aqueous ethanolic extraction process after separating the solvents from it which yielded (85%). Where notice that the pH of the extract is almost neutral, while the productivity was very good, and this may be due to the use of a mixture of solvents instead of one, as well as the difference in the polarity between them, as the water is more polarity than ethanol.

Qualitative determination of phytochemical screening

As shown in table 2, the results of the quantum test for the ingredients (secondary metabolites) present in the *Marrubium vulgare* L leaves extract were both of the alkaloids, flavonoids, tannins and saponins are present in the extract. In different parts of plants present several natural bioactive ingredients, which work as a defence against diseases for the plants or for who will nutrients on it. Or could use as benefits to decrease the danger of several illnesses such as diabetes, high blood pressure, stroke, cancer, heart disease. Flavonoids present in *Marrubium vulgare* L leaves may act as an anti-inflammatory agent. Also, it is possible to use the leaves of this plant to reduce and prevent the damage caused by the presence and formation of free radicals in the human body, as well as an antipyretic, antispasmodic, and a treatment to stop diarrhea. The tannins act as a catalyst for the activity of the immune system, In addition, The presence of tannin in the extract of this plant is of vital importance, as it prevents the production of bacterial proliferation, meaning that the higher the amount of tannin present in the plant, the more effective against bacteria [13,14]. Glycosides or tri-terpenoid saponins are important phytochemical composites with diverse activities such as anti-allergic, antiviral, antifungal potentials.

***Marrubium vulgare* L**		
Composites	**Tests**	**Results**
Alkaloids	Hager's	+
	Wagner's	+
Flavonoids	Ammonia	+
	Ammonium Chloride	+
Tannins	Mitchell's	+
	Vanillin hydrochloric acid	+
Saponins	Froth	+
	Olive's oil	+

Table 2: Results of the Qualitative determination of phytochemical screening.

Quantitative determination of phytochemical screening

The quantitative estimation considered as fundamental parameters in establishing the standard for raw medicines. The solvent used in extraction could present a system of giving preceding knowledge on the nature of the medication. As showed in table 3 the results of the quantitative test of *Marrubium vulgare* L leaves extract, the results for alkaloids, flavonoids and saponins were 56.86, 67.35 and 71.83%, respectively. Therefore, that saponins> flavonoids> alkaloids as quantitatively were presents in the extract. Tannins in its structural include large amounts of phenolic rings and classified into groups hydrolyzed and condensed tannins. The hydrolysed tannins are a mixture of simple phenols linked by ester, while, the condensed tannins have consisted of flavonoids members with many levels of condensation [15].

Physico-chemical analysis

Physical evaluation

As shown in table 4 the leaves of *Marrubium vulgare* L., have a greenish-grey leaf, with a densely crinkled surface, and are covered in downy hairs. The leaves have turned colour to light brown after drying, as well as grinding. This aromatic taste bitter smells similar to the essence of musk.

Characterizations of leaves of *Marrubium vulgare* L.							
Taste		**Colure**		**Shape**		**Odor**	
Fresh Leaves	**Dry Leaves**	**Fresh Leaves**	**Dry Leaves**	**Fresh Leaves**	**Dry Leaves**	**Fresh Leaves**	**Dry Leaves**
Bitter, aromatic	Bitter, aromatic	greenish-grey with fluff	Pale Browne	greenish-grey with fluff	Soft and Pale Browne	Musky	Pungent yet pleasant

Table 4: Characterizations of *Marrubium vulgare* L. leaves

Physico-chemical parameters of *Marrubium vulgare* L. (% w/w)		
Moisture Content		11.26
Loss on Drying		19.10
Total Ash value		13.40
Water-Soluble Ash		7.90
Acid-Insoluble Ash		10.48
Alcohol-Soluble Extractive		8.31
Solubility	H_2O	Partially: 4.37
	Ethanol	Partially: 5.67
	Chloroform	Insoluble
	Ether	Insoluble

Table 5: Physico-chemical parameters of *Marrubium vulgare* L. leaves.

The results of physicochemical analysis of leaves of *Marrubium vulgare* L. medicinal plant are shown in table 5 were the moisture Content was, loss on drying, total ash value, water-soluble Ash, acid-insoluble ash and alcohol-soluble extractive were 11.26, 19.10, 13.40, 7.90, 10.48 and 8.31, respectively. While were each of the solubility partially (4.37%) in water, partially (5.76%) in Ethanol, insoluble in chloroform and in ether. Where, the solubility of ash in the water is a good indication of a correct method of extraction for salts that are soluble in water during drugs preparation, or rather also important for being aware of contamination or likewise wrong handling of medicines. The water-soluble ash, total ash and acid-insoluble ash and the ash value these are various procedures for the determination of the total ash which are used to determine the total quantity of matter combustion after burning [16]. While acid insoluble-ash reveals pollution with silica, which leads to a correlation of this with the Total Ash value of the corresponding sample

and will distinguish between polluting matters and changes of the natural ash of the medicine. The extractive values are illustrative of the appearance of the polar or nonpolar extractable composites in plant matter. Moisture is an obligatory ingredient of crude medicines, which must be reduced as far as possible, where were if inadequate drying begins to decay by microbes and offers perhaps the enzymatic removal of energetic values [17].

The results of each weight loss, the rates CR, surface coverage (θ) and inhibition efficiency% (EI) for each coupon in the presence and absence of *Marrubium vulgare* L. extract in acid medium HCL 0.5M and base medium NaOH 0.5M.

Study of weight loss for aluminums coupons in the presence and absence of *Marrubium vulgare L.* extract in acid and base mediums.

Inhibitor Conc. g/l (%)	Initial Weight of Metals (g/cm^2) W_1	Weight of Metals after 24 h. (g/cm^2)	Weight of Metals after 48 h. (g/cm^2)	Weight of Metals after 72 h. (g/cm^2) W_2
0	1.6742	1.3527	1.0452	0.8354
25	0.2086	0.2058	0.2118	0.4236
50	0.9534	0.9351	0.9440	1.888
75	1.4977	1.4855	1.4790	2.978
100*	1.9813	1.9850	1.9839	3.9678

Table 6: Results of the weight loss study for aluminums coupons in the presence and absence of *Mrrubium vulgare* L. extract in acid medium HCL 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Inhibitor Conc. g/l (%)	Initial Weight of Metal (g/cm^2) W_1	Weight of Metal after 72 h. (g/cm^2) W_2	Weight loss W_1-W_2	Corrosion rate gcm^{-2}h^{-1} (× 10^{-4})	Surface coverage (θ)	Percent Inhibition Efficiency IE (%) η
0	1.6742	0.8354	0.8388	0.00466	0	0
25	0.2086	0.4236	0.2150	0.0012	0.74	74
50	0.9534	1.888	0.9346	0.0052	0.12	12
75	1.4977	2.978	1.4803	0.0051	0.10	10
100*	1.9813	3.9678	1.9865	0.0069	0.48	48

Table 7: Results of the study of weight loss, the rates CR, surface coverage (θ) and inhibition efficiency% (EI) for aluminums coupons in the presence and absence of *Mrrubium vulgare* L. extract in acid medium HCL 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Table 6 and 7 and as well as figure 1 presented the results of the study of weight loss, corrosion rate, calculation of surface coverage and inhibition efficiency for aluminium coupons in the presence and absence of *Marrubium vulgare* L extract in acidic medium HCL 0.5M at different concentrations. Where the medium concentrations were 0, 25, 50, 75 and 100% (the extract only 100% without mixing it with the acid medium) and the weights obtained after immersion in the concentrations medium were 1.6742, 0.2086, 0.9534, 1.4977 and 1.9813 g/cm^2, respectively. Wherever notice that the loss in the weight loss of the aluminum coupons' is very small compared to the weight loss in other concentrations, which were 0% concentration, and which means that the medium of immersion was acidic without adding the plant extract of *Mrrubium vulgare* L leaves 1.6742, 1.3527 1.0452 and 0. 8354 g/cm^2 g/cm^2, and for a concentration of 25%, the results were 0.2086, 0.2058, 0.2118 and 0.4236 g/cm^2. The concentration 50% and its results were 0.9534, 0.9351, 0.9440 and 1.888 g/cm^2. The concentration of 75% of the acid medium 1.4977, 1.4855, 1.4790 and 1.978 g/

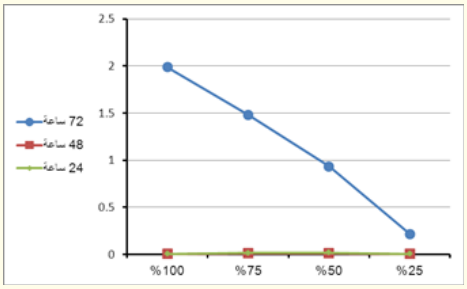

Figure 1

cm^2; respectively, were within 24, 48 and 72 hours of immersion for all tested coupon's samples. From this, that report the greater the concentration of the plant extract in the medium, the less weight loss of the metal sample (aluminum). The charts showed that the corrosion rate decreases in the presence of the inhibitor and the inhibition efficiency increases with increasing concentration. As the following corrosion rate results show this more than 0.00466, 0.0012, 0.0052, 0.0051 and 0.0069 g cm^{-2} x $^{-1}$ (X 10^{-4}); for each of the concentrations 0, 25, 50, 75 and 100%, and the surface coverage increased with increasing the concentration. As for the efficiency and coverage of the surface, it increased with increasing concentration. (Surface coverage) was as follows: 0, 0.74, 0.12, 0.10 and 0.48 for concentrations 0, 25, 50, 75 and 100%. Thus, it is clear that the inhibition efficiency (IE% 0, 74, 12, 10 and 48%. It turned out that all the reactions explain the adsorption isomers, that is, the degree of interaction of the different inhibitor molecules with the metal surface. And because inhibition of corrosion by using an organic inhibitor occurs with the development of protective layers (films) resulting from adsorbed extracts particles on metal surfaces. It is also known that oxidation is the reduction of electrons, the excess of oxygen, or the reduction of hydrogen in any element. This reaction is responsible for the actual attrition of any material or corrosion of the metal. Aluminium and its alloys are extremely important in many industrial and domestic applications, due to their passivity to corrosion in neutral media and atmospheric conditions and also due to the formation of a negative oxide layer on them. Although it reacts in many media, it becomes negative upon exposure to water and the atmosphere and dissolves in hydrochloric acid and releases H_2 gas. And as an example by the following equation:

$$2Al + 6\,HCl + 12\,H_2O_2 \longrightarrow [Al\,(H_2O)\,6]\,Cl_3 + 3H_2$$

In addition to this, the presence of some compounds that contain heterocyclic atoms such as N and SO in the plant extract, which act as good inhibitors that may increase the basicity of the medium and more extra cause electron density and thus help prevent corrosion. And these heterocyclic atoms like O, N and S considered active centers of the adsorption process on the metal surface. It is important also that the size, orientation, shape, and electrical charges of the molecule, which additionally play a role in the effectiveness of inhibition. It is worth noting that corrosion not only inflicts heavy losses on the country's economy, but it also represents a major threat to human safety. The plants' natural products are environmentally friendly, compatible, non-polluting, less toxic, readily available, biodegradable, and economical to use as corrosion inhibitors. These inhibitors contain many alkaloids that are regular to N, O and S which are absorbed on the mineral surface, which basically prevent the conferring of H + and thus leads to decay metal ions. Consequently, and seemingly, the extract of different parts of the *Marrubium vulgare* L plant such as leaves, seeds, stems and bark can be used, i.e. used as a dampener to reduce the rate of corrosion of the metal such as aluminium in the acidic medium. Furthermore, as shown in table 6, 7 and figure 1 the inhibition efficiency increases with increasing acid resistance and likewise increases with increasing the concentration of leaf extract of *Marrubium vulgare* L. And that the degree of surface coverage of the metal covered with retarder absorption to prevent active sites on the surface with different concentrations of the inhibitor for different concentrations of hydrochloric acid, which is shown in table 7 of the papers. Where it appears that the degree of surface coverage increases with increasing the concentration of the inhibitor, however, at a concentration of 75%, the coverage is less than that of 25%. However, it is important to note that there is an inhibition efficiency present due to the use of the natural inhibitor against corrosion of the metal, and it is possible to explain and reveal more than the presence of some weights for the stiff metal parts and this deviation in the behaviour of the unit, based on the interaction of the particles absorbed on the surface of the metal. More than that, the adsorbent layer is monomolecular, that is, there is no interaction between adsorbed molecules themselves and between adsorbate and adsorbent molecules. That is, only then is the gradient

Inhibitor Conc. g/l (%)	Initial Weight of Metals (g/cm^2) W_1	Weight of Metals after 24 h. (g/cm^2)	Weight of Metals after 48 h. (g/cm^2)	Weight of Metals after 72 h. (g/cm^2) W_2
0	1.52896	1.4011	1.2013	0.3023
25	1.4640	0.6948	0.2280	0.1973
50	1.6758	1.1192	0.9550	0.1012
75	1.8116	1.5527	1.5134	1.5212
100*	1.9809	1.9827	1.9832	1.6842

Table 8: Results of the weight loss study for aluminums coupons in the presence and absence of *Mrrubium vulgare* L. extract in alkali medium NaOH 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Inhibitor Conc. g/l (%)	Initial Weight of Metal(g/cm^2) W_1	Weight of Metal after 72 h. (g/cm^2) W_2	Weight loss W_1-W_2	Corrosion rate gcm^{-2}h^{-1} (× 10^{-4})	Surface coverage (θ)	Percent Inhibition Efficiency IE (%) η
0	1.52896	0.3023	1.22666	0.0043	0	0
25	1.4640	0.1973	1.26670	0.0044	0.023	2.3
50	1.6758	0.1012	1.5746	0.0055	0.279	27.9
75	1.8116	1.5212	0.2904	0.00101	0.765	76.5
100*	1.9809	1.6842	0.2967	0.00103	0.760	76

Table 9: Results of the study of weight loss, the rates CR, surface coverage (θ) and inhibition efficiency % (EI) for aluminums coupons in the presence and absence of *Mrrubium vulgare* L. extract in acid medium NaOH 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

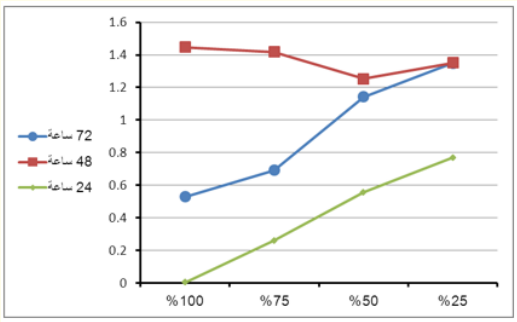

Figure 2

the unit but in actual practice, there is an interaction between the adsorbent molecules themselves and between the adsorbate and adsorbent molecules and this is the reason why the gradient is not a unit. In the tables, a contrast is shown with the concentration of the leaves extract of the acidic medium HCl. That is, in reality, there is an interaction between the molecules of the adsorbents themselves and between the molecules of adsorbents and adsorbate and this is the reason why the gradient in weights is not a unit.

Table 8, 9 and figure 2 showed, the results of a weight-loss study for aluminium coupons in the presence and absence of *Marrubium vulgare* L extract in the alkali medium NaOH 0.5 M in different concentrations where the concentrations were 0, 25, 50, 75 and 100 at time 24, 48 and 72 hours, first for the alkali medium and without adding the plant extract, meaning that the concentration was 0%, so it was 1.4011, 1.2013 and 0.3023 g/cm^2, respectively, where notice the very large loss in the weight of the aluminium metal coupons with the increase in the immersion time. The metal was immersed in the alkali medium, and the concentration of 25% was: 1.4640, 0.6948, 0.2280 and 0.1973 g/cm^2, respectively, and the 50% concentration were 1.6758, 1.1192 0.9550 and 0.1012 and the concentration 75% was 1.8116, 1.5527, 1.5134 and 1. 5212, and the concentration of 100% were 1.9809,1.9827, 1.9832 and 1.6842 respectively, as a note that the loss in the weight of aluminium cou-

pons during the time from 24 to 72 hours is very large, for example, at 0% concentration (which is in the absence of the plant extract), this weight loss was as shown in Table 8 was 1.22666 g/cm^2, this is compared to the loss of the weight of the coupon submerged in the extract only, i.e. 100%, which was 0.2967 g/cm^2, It also means that the presence of the extract had a large and very effective function in protecting the metal coupons from corrosion as the weight loss in the metal was very small. That is, the higher the concentrations of the plant extract in the medium the less weight loss of the metal (aluminium) coupons. Based on what was previously mentioned, it is possible to know that what are attributed to the lower corrosion rate and the increase in the inhibition efficiency are due to the fact that the inhibitor is adsorbed onto the surface of the metal. As the metal adsorbs the natural extract it creates a barrier that prevents corrosion [18-20]. The compounds of the secondary metabolites, such as alkaloids, phenols and saponins, whose are compounds found in the leaves of the *Marrubium vulgare* L plant, that contain heterocyclic atoms such as oxygen, which have free lone-pair electrons, may be responsible for such adsorption.

As shown in tables 10 and 11, as well as figure 3, the results of the study of weight loss, corrosion rate, calculation of surface coverage and inhibition efficiency for copper coupons in the presence and absence of *Marrubium vulgare* L extract, in acidic medium HCL 0.5 M in different concentrations, where the concentrations were 0, 25, 50, 75 and 100% and the weights obtained after immersion in the concentration of the extract only 100% without mixing it with the acid medium were 4.6480, 4.6494 and 4.6495 g/cm^2, respectively. Wherever notice that the weight loss of copper coupons is very small compared with the weight loss in other concentrations, that was 0% concentration, and which means that the immersion medium was acidic without adding the plant extract of *Marrubium vulgare* L. leaves to it, 3.9293, 3.0374 and 3.0012 g/cm^2, and for the concentration of 25%, the results were 4.4516, 4.4465 and 4.4417 g/cm^2. While the 50%, concentration results were 3.5523, 3.5513 and 3.5523 g/cm^2, and the 75% concentration results are 4.1172, 4.1178 and 4.1111 g/cm^2; Respectively, within 24, 48 and 72 hours for all tested coupons. That is, the higher the concentration of the

Inhibitor Conc. g/l (%)	Initial Weight of Metals (g/cm^2) W_1	Weight of Metals after 24 h. (g/cm^2)	Weight of Metals after 48 h. (g/cm^2)	Weight of Metals after 72 h. (g/cm^2) W_2
0	4.3821	3.9293	3.0374	3.0012
25	4.4521	4.4516	4.4465	4.4417
50	3.5557	3.5523	3.5513	3.5523
75	4.1175	4.1172	4.1178	4.1111
100*	4.6465	4.6480	4.6494	4.6495

Table 10: Results of the weight loss study for cupper coupons in the presence and absence of *Mrrubium vulgare* L. extract in Acid medium HCl 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Inhibitor Conc. g/l (%)	Initial Weight of Metal(g/cm^2) W_1	Weight of Metal after 72 h. (g/cm^2) W_2	Weight loss W_1-W_2	Corrosion rate gcm^{-2}h^{-1} (× 10^{-4})	Surface coverage (θ)	Percent Inhibition Efficiency IE (%) η
0	4.3821	3.0012	1.3809	0.0050	0	0
25	4.4521	4.4417	0.0351	0.00012	0.976	97.6
50	3.5557	3.5523	0.0034	0.00002	0.996	99.6
75	4.1175	4.1111	0.0064	0.00002	0.996	99.6
100*	4.6465	4.6495	0.0030	0.00001	0.998	99.8

Table 11: Results of the study of weight loss, the rates CR, surface coverage (θ) and inhibition efficiency % (EI) for cupper coupons in the presence and absence of *Mrrubium vulgare* L. extract in acid medium HCl 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

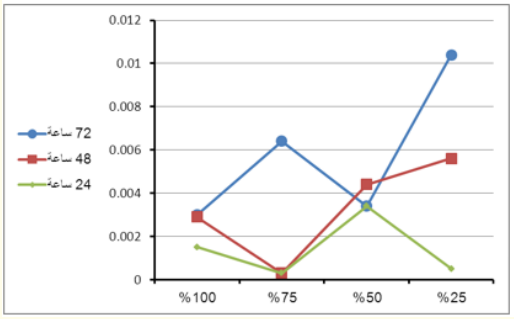

Figure 3

plant extract in the medium, the less weight of the metal coupons (copper) was lost, and the charts showed that the corrosion rate decreased in the presence of the inhibitor and the inhibition efficiency increased with increasing concentration. As the following corrosion rate results show more than 0.0050, 0.00012, 0.00002, 0.00002 and 0.00001 g cm^{-2} x-1 (X 10^{-4}); g $cm^{-2}h^{-1}$ (x 10^{-4}), for each of the concentrations 0, 25, 50, 75 and 100%, that is, with the increase in the concentration of the extract, the surface coverage increased. As for the efficiency of coverage, it increased with increasing concentration, (surface coverage) and it was as 0.976, 0.996, 0.996 and 0.998 for concentrations 0, 25, 50, 75 and 100%. Therefore, it is clear that the inhibition efficiency (EI%) 0, 97.6, 99.6, 99.6 and 99.8%, respectively, and from this, that the greater the concentration of the plant extract in the medium, the less weight loss of the metals (copper) coupons, and that the weight loss was very slight compared to what happened with aluminium coupons.

Inhibitor Conc. g/l (%)	Initial Weight of Metals (g/cm^2) W_1	Weight of Metals after 24 h. (g/cm^2)	Weight of Metals after 48 h. (g/cm^2)	Weight of Metals after 72 h. (g/cm^2) W_2
0	3.5421	3.3621	3.1034	3.0567
25	3.8519	3.8056	3.7433	3.1523
50	3.3512	3.3427	3.2956	3.2112
75	3.1822	3.1812	3.1730	3.1020
100*	3.1115	3.1122	3.1139	3.3101

Table 12: Results of the weight loss study for cupper coupons in the presence and absence of *Mrrubium vulgare* L. extract in alkali medium NaOH 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Inhibitor Conc. g/l (%)	Initial Weight of Metal(g/cm^2) W_1	Weight of Metal after 72 h. (g/cm^2) W_2	Weight loss W_1-W_2	Corrosion rate $gcm^{-2}h^{-1}$ (× 10^{-4})	Surface coverage (θ)	Percent Inhibition Efficiency IE (%) η
0	3.5421	3.0567	0.4854	0.0017	0	0
25	3.8519	3.1523	0.6996	0.0024	0.412	41.2
50	3.3512	3.2112	0.1400	0.00049	0.71	71
75	3.1822	3.1020	0.0802	0.00028	0.84	84
100*	3.1115	3.3101	0.1986	0.00069	0.60	60

Table 13: Results of the study of weight loss, the rates CR, surface coverage (θ) and inhibition efficiency% (EI) for cupper coupons in the presence and absence of *Mrrubium vulgare* L. extract in alkali medium NaOH 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

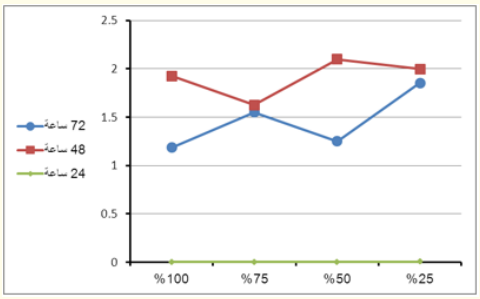

Figure 4

As shown in table 12, 13 and figure 4, the results of the weight loss study for copper parts in the presence and absence of *Marrubium vulgare* L extract in the alkali medium and in different concentrations where the concentrations were 0, 25, 75 and 100% and the weights obtained during 24, 48 and 72 hours for all metal coupons in the alkali medium only and without mixing it with the plant's extract, i.e. 0% is 3.5421, 3.3621, 3.1034 and 3.0567 g/cm^2; As for the concentration of 25% of the extract, the results were 3.8519, 3.8056, 3.7433 and 3.1523 g/cm^2, and for the concentration 50% of the extract, results were 3.3512, 3.3427, 3.2956 and 3.2112 g/cm^2. The concentration 100% of the extract i.e. the extract only and without mixing it with the alkali medium, its results were 3.1115, 3.1122, 3.1139 and 4.6495 g/cm^2, previously. From these results, it is clear that the higher the concentration of the plant extract in the medium, the less weight loss of the metals coupons (copper). And that the weight loss was very slight compared to what happened with aluminium coupons. Figure 4 showed that the corrosion rate decreased in the presence of the inhibitor as the inhibition efficiency increased with increasing concentration. The following corrosion rate results illustrate this more: 0.0017, 0.0024, 0.00049, 0.00028 and 0.00069 g cm^{-2} x^{-1} (X 10^{-4}); for each of the concentrations 0, 25, 50, 75 and 100%, that is, with increasing the concentration of the extract, the surface coverage increased very slightly, as for the efficiency of coverage, it increased with increasing concentration. (Surface coverage) were as follows: 0, 0.412, 0.71, 0.84 and 0.60 for concentrations 0, 25, 50, 75 and 100%, respectively. Therefore, it becomes clear that the inhibition efficiency (IE% 0, 41.2, 71, 84 and 60%, each, and from this results that the higher the concentration of the plant extract in the medium, the less weight loss of the metal coupons (copper), and that the weight loss was very slight compared to what happened with aluminium coupons.

Inhibitor Conc. g/l (%)	Initial Weight of Metals (g/cm^2) W_1	Weight of Metals after 24 h. (g/cm^2)	Weight of Metals after 48 h. (g/cm^2)	Weight of Metals after 72 h. (g/cm^2) W_2
0	19.5801	19.3592	19.0137	18.8512
25	20.1524	20.0972	20.0187	19.9860
50	19.4730	19.3500	19.3250	19.3180
75	20.3098	20.1940	20.1792	20.1500
100*	19.7614	19.7740	19.7970	19.7750

Table 14: Results of the weight loss study for iron coupons in the presence and absence of *Mrrubium vulgare* L. extract in acid medium HCl 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Inhibitor Conc. g/l (%)	Initial Weight of Metal(g/cm^2) W_1	Weight of Metal after 72 h. (g/cm^2) W_2	Weight loss W_1-W_2	Corrosion rate gcm^{-2}h^{-1} (× 10^{-4})	Surface coverage (θ)	Percent Inhibition Efficiency IE (%) η
0	19.5801	18.8512	0.7289	0.0025	0	0
25	20.1524	19.9860	0.1664	0.0006	0.76	76
50	19.4730	19.3180	0.1550	0.0005	0.80	80
75	20.3098	20.1500	0.1598	0.0005	0.80	80
100*	19.7614	19.7750	0.0136	0.0001	0.96	96

Table 15: Results of the study of weight loss, the rates CR, surface coverage (θ) and inhibition efficiency % (EI) for iron coupons in the presence and absence of *Mrrubium vulgare* L. extract in acid medium HCl 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

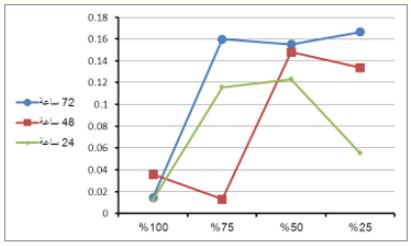

Figure 5

As shown in table 14, 15 and figure 5, the results of the weight loss study for iron coupons in the presence and absence of *Marrubium vulgare* L extract in the acidic medium and in different concentrations where the concentrations were 0, 25, 75 and 100% and the weights obtained within 24, 48 and 72 hours, for all coupons in acidic medium only and without mixing it with the extract, i.e. 0% are 19.3592, 19.0137 and 18.8512. g/cm^2; As for the concentration of 25% of the extract, the results were 20.0972, 20.0187 and 19.9860 g/cm^2. The results of concentration 50% of the extract were 19.3500, 19.3250 and 19.3180 g/cm^2. As for the concentration of 100% of the extract, i.e. the extract only, without mixing it with acid medium, its results were 19.7740, 19.7970 and 19.7750 g/cm^2. From these results, it is clear that the higher the concentration of the plant extract in the acid medium, the less weight loss of the metals coupons (copper). The figure showed that the corrosion rate decreased with an inhibitor, and the inhibition efficiency increased with increasing concentration. Since the results show the following corrosion rate: 0.0025, 0.0006, 0.0005, 0.0005 and 0.0001 g cm^{-2} s^{-1} (X 10^{-4}); for each of the concentrations 0, 25, 50, 75 and 100%, that is, with increasing the concentration of the extract, the surface coverage increased very slightly. As for the coverage efficiency, it increased with increasing concentration. (Surface coverage) were as follows: 0, 0.76, 0.80, 0.80 and 0.96 for concentrations 0, 25, 50, 75 and 100%. Therefore, it is clear that the inhibition efficiency (IE %) 0, 76, 80, 80 and 96%, respectively, and from this that the higher the concentration of the plant extract in the acid medium, the lighter weight loss of the metal coupons (iron). It is possible by using the heat content of the interaction (*Enthalpy*) Δ H, to find out the number of moles of iron, and thus the number of moles of hydrochloric acid, which participated in the interaction. From it, it is possible to know the number of moles of hydrogen gas resulting from the reaction. That is, it is possible to use the molar volume of gas in STP to calculate the volume of hydrogen gas, and according to Avogadro's law, the volume of one mole of any gas at Standard Temperature and Pressure (STP = 273 K and 1 atm) is 22.4 L. or may as : the molar volume, or *volume of one mole of gas*, depends on pressure and temperature, and is 22.4 liters - at 0°C (273.15 K) and 1 atm (101325 Pa), or STP (Standard Temperature and Pressure), for every gas which behaves similarly to an ideal gas. The ideal gas molar volume increases to 24.0 liters as the temperature increases to 20 °C (at 1 atm).

$Fe\ (s) + 2HCl\ (aq.) \rightarrow FeCl_2\ (aq.) + H_2\ (g)\ \Delta H = -87.9\ kJ.$

The Enthalpy (H) is the enthalpy of a system under constant pressure. That is, the heat that is absorbed or released through a reaction at a constant pressure, which is the same as the variable temperature in enthalpy, is given the symbol (ΔH, Enthalpy).

Inhibitor Conc. g/l (%)	Initial Weight of Metals (g/cm^2) W_1	Weight of Metals after 24 h. (g/cm^2)	Weight of Metals after 48 h. (g/cm^2)	Weight of Metals after 72 h. (g/cm^2) W_2
0	19.2034	18.9418	18.7103	18.6418
25	20.1525	20.1597	20.1625	19.9103
50	19.4750	19.4905	19.5006	19.0143
75	20.3132	20.3300	20.314	20.2901
*100	19.7567	19.7738	19.7848	20.0121

Table 16: Results of the weight loss study for iron coupons in the presence and absence of *Mrrubium vulgare* L. extract in alkali medium NaOH 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

Inhibitor Conc. g/l (%)	Initial Weight of Metal(g/cm^2) W_1	Weight of Metal after 72 h. (g/cm^2) W_2	Weight loss W_1-W_2	Corrosion rate $gcm^{-2}h^{-1}$ ($\times 10^{-4}$)	Surface coverage (θ)	Percent Inhibition Efficiency IE (%) η
0	19.2034	18.6418	0.5616	0.00195	0	0
25	20.1525	19.9103	0.2422	0.00084	0.0011	0.11
50	19.4750	19.0143	0.4607	0.0016	0.18	18
75	20.3132	20.2901	0.0231	0.00008	0.96	96
100*	19.7567	20.0121	0.2554	0.00009	0.95	95

Table 17: Results of the study of weight loss, the rates CR, surface coverage (θ) and inhibition efficiency% (EI) for iron coupons in the presence and absence of *Mrrubium vulgare* L. extract in alkali medium NaOH 0.5 M.

* = Plant extract only, 0 = immersion medium in the absence of the extract.

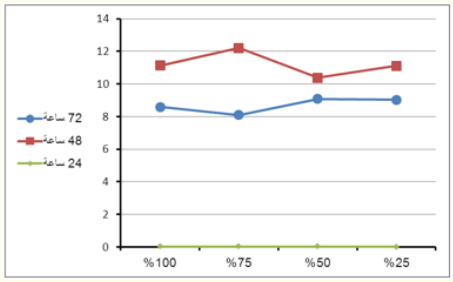

Figure 6

As shown in table 16, 17 and figure 6, the results of the weight loss study of coupons iron in the presence and absence of *Marrubium vulgare* L extract in the alkali medium and in different concentrations where the concentrations were 0, 25, 75 and 100% and the weights obtained within 24, 48 and 72 hours, for all coupons as follows in alkali medium only and without mixing it with the extract i.e. 0% are 18.9418, 18.7103 and 18.6418 g/cm^2, individually; As for the concentration of 25% of the extract, the results were 20.1597, 20.1625 and 19.9103 g/cm^2, respectively. The concentration was 50% of the extract, and the results were 19.4905, 19.5006 and 19.0143 g/cm 2, sequentially. As for the concentration of 100% of the extract, i.e. the extract only, without mixing it with the base medium, its results were 19.7738, 19.7848 and 20.0121 g/cm^2, each. Accordingly, these results it is clear that the higher the concentration of the plant extract in the alkali medium, the less weight loss of the metals coupons (iron). Figure 6 showed that the corrosion rate decreased with an inhibitor, and the inhibition efficiency increased with increasing concentration. As the following corrosion rate results show this more than 0.00195, 0.00084, 0.0016, 0.00008 and 0.00009 $g/cm^{-2}\ x^{-1}$ (X 10^{-4}), for each of the concentrations 0, 25, 50, 75 and 100%, that is, with increasing the concentration of the extract, the surface coverage increased very slightly. As for the efficiency of coverage, it increased with increasing concentration. (Surface coverage) were as follows: 0, 0.0011, 0.18, 0.96 and 0.95 for concentrations 0, 25, 50, 75 and 100%. Therefore, it is clear that the inhibition efficiency (IE %) 0, 0.11, 18, 96 and 95%, respectively, hence that the higher the concentration of the plant extract in the alkali medium, the less weight loss of the metal coupons (iron).

Inhibition efficiency (IE %)

The effect of time on Inhibition Efficiency (IE %) was studied, where the inhibiting the metal corrosion in acid and alkali media. and while the values of IE% increased athwart the time of immersion, due to the adsorption. And the adsorption happening between the covering particles and the metal surface, therefore, coupons were subjected to mass loss measurements at prolonged immersion times (up to 72h), to control the direction of inhibition which IE% values were continued to increase. Which also means the covering of the metals coupons area was continued with increasing of immersion time for it. That is, it is possible to the understanding that the higher inhibitory property of the inhibitors is due to the presence of p electrons in the aromatic rings, where that the presence of heterocyclic atoms such as oxygen, sulfur, and nitrogen, and the larger molecular size leads to it covering the largest area of the metallic surface. Besides, the results obtained indicate that the increase of inhibitors reduces the anodic dissolution of iron as well as the cathodic hydrogen evolution reaction. It also determined the

interaction of inhibitor molecules with the metal surface during the corrosion inhibition process, whether in the presence or absence of inhibitors of the metal samples, as they showed that the metal samples submerged in 0.5 N HCl were severely damaged by the violent acid attack. It also shows a relatively smooth surface of the metal after adding the natural inhibitor to the 0.5 N HCl solutions. That is, it can be concluded that the inhibitor molecules slow down the dissolution of the metal by forming an organic layer on the iron surface. Therefore, retarders protect the metal from the acidic or alkaline solution. In this research, the changes that occur on the surface of metals coupons such as aluminium in a solution of 0.5 M Na OH were observed in the absence and in the presence of a natural inhibitor, the *Marrubium vulgare* L extract from the beginning of the immersion time, where it is actually noticed that the surface of the metal coupons had cavities resulting from corrosion and are visible on the surface of the coupons. Probably, due to the aggressive ions, it was also observed that this corrosion damage was reduced and lost on the face of the metal coupons in the presence of the natural inhibitor in the alkali solution. It was observed that the surface morphology of the coupons exposed in acid and alkaline solutions with different concentrations of the extract, i.e. the higher the concentration of the extract, the less corrosion of metal pieces. This indicates that the insulating layer develops by the inhibitor on the metal surface coupons as it acts as a barrier against corrosion attack by these acid and alkaline solutions. Specifically, And it is evident that the extract of the *Mrrubium vulgare* L leaves used in this research consists of a mixture of natural chemical compounds Phytochemicals). Whosesoever these components of the aqueous extract act as an inhibitor of metal corrosion in acidic and alkaline solutions due to the adsorption of the various chemicals present in the extract and possibly through the pair of electrons of pi, in which the electrons interact with the vacant d orbital present in iron, for example. To clarify, the heterocyclic "O" atom and pi electrons of the organic compounds act as reaction sites in the adsorption process. It is also clear that the inhibition of metal corrosion mediated by the extract may be attributed to the adsorption of naturally available organic structures containing O or pi electrons in their molecules. Hence, this phenomenon of inhibition is very complex due to the presence of a mixture of chemical components. According to previous studies [21-30]. For instance, in the ethanol extract of pomegranate peels, where it contained compound limonene as the main compound, which is a cyclic alkene, in which it was proved and explained that due to the calculated free energy change Gads was between 23 and 30 kJ moll 1, it is clear that the reactions of the extract with the metal surface are neither ionic nor chemical reactions. Hence, this may be attributed to the interaction of the electron pi to an alkene on the metal surface through a physical process. In addition to this, inhibition has been adopted mainly due to the presence of organic compounds containing heterocyclic atoms. The formation of a protective layer was observed due to the adsorption of the retarder compounds on the surface of the metal. This prevents ionic diffusion towards or from the surface of the metal. The interference molecules are exchanged with the absorbent H_2O molecules on the metal surface to protect it from a further attack of the aggressive electrolytes. This barrier effect reduces the metal atoms involved in the electrochemical process and thus increases the effectiveness of corrosion. From the previous studies [62-58] also, results of measurements at pH using other aluminium corrosion inhibitors, as this effect is attributed to the electric point or IEP effect of the aluminium pH (at the pH 9) [31]. At a pH of 8 (less than IEP) the aluminium surface is positively charged, while at pH 10 (above IEP) the surface is negatively charged and in this paper, an aqueous solution containing other ions can lead to a lot of negatively charged ions. Systemically is instability due to the charge repulsion.

The solvent effect

Since several solvents can be used to obtain the natural extracts from plants, the function of the inhibition efficiency of the different extract obtained is another interesting topic. This synergistic effect could be related to its high potency for extracting active chemicals compounds from plants which are in turn responsible for the inhibitory effect. Hence, different solvents should experiment in order to determine which solvents obtain from the extract with the most immeasurable inhibition performance against corrosion. And in this research, two types of diffusions were used, which are distilled water and as ethyl alcohol to obtain the largest amount of chemical components, which should play an effective role with the best performance required. For example, alkaloids compounds, it is through their antioxidant properties and their collections associated polyphenols are expected to help protect the surface of the metal, where alkaloids acting as a good corrosion inhibitor because it contains nitrogen atoms. Moreover, it contains functional groups that are rich in oxygen compared to other groups, which

makes them more suitable for protecting the metal surface. Along with this, and as it was revealed in previous studies that the performance of the extracts obtained with different extraction solvents in the following order: ethanol > methanolic > aqueous and that this trend is a result of improving the efficiency of ethanol and methanol to extract the flavonoids present in the leaves of *Pterocarpus santalinoides* plant, they are well-known compounds that act as good inhibitors in carbon steel [32]. Likewise, the presence of aromatic cyclic compounds, especially those associated with host groups, have a role as corrosion inhibitors [33]. That is, by using different methods to obtain different inhibitors that protect the metal from corrosion, and in contrast, the inhibition efficiency increases with increasing the concentration of the inhibitor, such as the presence of a group of active compounds such as tannins, flavonoids and phenols in the extract. For the most part, it may be assumed that other functional groups, such as the carboxyl, hydroxyl, and carbonyl from the phenolic compounds in the extract on the surface of the metal, are both physically and chemically adsorbed, as a consequence, the electrostatic interactions and the covalent bonding between them, specifically, between the metal surface and these groups [34]. Too, that is it may be noted that the inhibitor molecules may contain pairs of electrons available for nucleophile interactions, through what is known as chemical adsorption or (chemisorption), with the metal surface, meaning that it is possible to obtain physi-sorption through the electrostatic reaction, (Electrostatic Interaction) between the hetero-atoms and the Fe^{+2} atoms. Viz., it is possible to bond to the back (back-bonding) through the electrons of the aromatic rings, it refers to the iron compounds that are divalent (oxidation state $^{+2}$). Furthermore, the products formed on the adsorbed particles from the metal surface explained that aromatic rings and heterocyclic atoms are the most suitable to be adsorbed on the metal surface, through the interactions between the donor and the acceptor of those electrons (Donor-Acceptor Interactions). And accomplishing to this, it is more probable the organic inhibitors containing heterocyclic atoms such as O, N and S are considered as a fundamental principle as explained and perceived in literature precisely because they have a higher electron density and thus act as a corrosion inhibitor. Also, means that O, N and S are the active centers of the adsorption process on the metal surface. Since the inhibition efficiency follows the sequence O <N <S <P, the use of organic compounds that contain oxygen and sulfur, especially nitrogen, and working to reduce the corrosion attack on metals, has a beneficial effect. Most organic inhibitors adsorb on the metallic surface by displacing water molecules on the surface and forming a compressive barrier. The availability of free electrons (free lone pair) and p electrons in the inhibitor molecules facilitate the electron transfer from the inhibitor to the metal, and from there a covalent bond can be formed that includes this transferring between them.

The results of hydrogen gas produced from the interaction of the metal coupons (iron - copper - aluminium) with the media used

Measuring the volume of hydrogen gas produced per unit time (20s)

The measured hydrogen volume can be converted into moles of grams using ideal gas laws. Simply assuming that the number of moles of developed hydrogen equals the number of moles of hydrogen in the solution used for immersion, the rate of weight loss or weight loss can be calculated for the coupon. Undoubtedly, the corrosion rate measured by hydrogen evolution is exactly equal to the rate of weight loss [35-37].

Table 18 shows the results of hydrogen produced from the reaction of iron coupons in the acid medium, where the weight loss of the iron pieces after conducting the electric current to the positive electrodes and the negative electrode were 0.1833 and 0.0072 g/cm^2, respectively, while the hydrogen product from this reaction was 170 g/cm^3. Where it is clear, that the weight loss of iron at the anode was the highest and that the volume of hydrogen gas produced from this loss resulting from the interaction of iron with hydrochloric acid, with a time of 20 seconds. And the results of hydrogen produced from the reaction of the iron pieces in the alkali medium, where the weight loss of the iron pieces after conducting the electric current to the anode and the negative electrode was 0.0159, 0.01 g/cm^2, respectively, while the hydrogen outcome from this reaction was 240 g/cm3, with a time of 20 seconds. While the aluminium coupons the results of hydrogen rising from the reaction of aluminium cutting in an acidic medium, where the weight loss of the iron pieces after conducting the electric current to the positive electrodes and the negative electrode was 0.0026, 0.0026

Metal's Name Coupon's Pole		Weight of Metal Coupon's after 20 Sec. (g/cm^2)	* Weight loss (g/cm^2) $W_1 - W_2$	Volume of H_2 ($g\ cm^3$)	Medium
Iron	Anode	7.6769	0.1833	170	Acid
	Cathode	7.6962	0.0072		
	Anode	7.7159	0.0195	140	Alkali
	Cathode	7.6664	0.1000		
Aluminium	Anode	1.6549	0.0026	150	Acid
	Cathode	1.1665	0.0036		
	Anode	1.6378	0.0085	180	Alkali
	Cathode	1.1675	0.0078		
Copper	Anode	4.3275	0.0075	80	Acid
	Cathode	4.6277	0.0038		
	Anode	4.6336	0.0112	40	Alkali
	Cathode	4.3248	0.0183		

Table 18: Results of hydrogen resulting from the reaction of metal coupons in acidic and alkali medium.

*The weight loss of coupon before immersion in the medium and Weight loss of coupons after immersion and connected to an electric source was calculated according to Weight loss (g/cm^2) = $W_1 - W_2$

g/cm^2, respectively, while the hydrogen produces from this reaction was 150 g/cm3, with a time of 20 seconds. And the results of hydrogen produced from the reaction of aluminium coupons in the alkali medium, where the weight loss after conducting the electric current to the positive electrodes and the negative electrode was 0.0085 and 0.0078 g/cm^2, respectively, while the hydrogen product from this reaction was 150 g/cm3, with a time of 20 seconds. As from the above results, can verify that more hydrogen is produced at the same time with higher alkaline concentration (hence, the reaction rate is higher). It is possible to compare with other metals and alkaline mediums with each other, it is noted that NaOH has a tendency to accelerate the reaction more effectively than the acid medium in addition to iron or copper pieces, especially with a larger metal thickness. The hydrogen results from coupons of copper reaction in the acidic, where the weight loss to cut copper after connecting the power supply poles positive and negative electrode were 0.0075 and 0.0038 g/cm^2, respectively, while the hydrogen produced from the interaction 80 g/cm^3, at a time of 20 seconds. Also as shown in table 16 the results of hydrogen rising from the reaction of copper coupons in alkaline medium, where the weight loss of the copper after conducting the electric current to the positive electrodes and the negative electrode were 0.0112 and 0.0183 g/cm^2, respectively, while the hydrogen production from this reaction was 40 g/cm^3, at a time. At 20 seconds. Note that if the copper is alone with sodium hydroxide, it will not react. This is principally true. Copper is completely unreactive, and sodium is highly reactive. To replace the sodium, the reaction will have very high activation energy. Thus it is theoretically possible to do this reaction, but obtaining the copper ion would be much cheaper and safer:

$$Cu^{2+}_{(aqus.)} + 2\ NaOH_{(aqus.)} \rightarrow Cu(OH)_{2\ (s)} + 2\ Na^{+}_{(aqus.)}$$

If the copper is present as a salt, it is called a sedimentation reaction, which gives a blue precipitate.

The crude extract of *Marrubium vulgare* L. showed reasonable to important antibacterial activity against four tested bacterial organisms as compared to the standard ciprofloxacin (10 µg/ml). The investigation exhibited that the crude extract of leaves was efficient against all types of bacteria (*Escherichia Coli, Klebsiella pneumonia, Proteus Vulgaris* and *Staphylococcus aureus*). Therefore, according to the results, it is indicated that the crude extract of *Marrubium vulgare* L., plant owned *in-vitro* antibacterial activity. From this, to conduct more inclusive analyzes of the active chemical compounds

Bacterial strains	Crude extract concentrations (%)				Antibiotic
	25	50	75	100	Ciprofloxacin (10 µg/ml)
Escherichia. Coli	-	+	++	+++	23
Klebsiella pneumonia	-	+	++	+++	22
Staphylococcus aureus	-	+	++	+++	21
Proteus vulgaris	-	+	++	+++	21

Table 19: The inhibition zone in mm of the crude extract *of Mrrubium vulgare* L on the growth of the bacterial strains.

Where the diameters of the inhibition zone measured in (mm), which mean that (-) no inhibition, (+) medium effect (8-10mm), (+++) strong effect (11-14 mm) and (++++) very strong effect (15-20mm).

existing in this plant to define and explain those diverse ingredients, and also, to verify the intensified effect of this plant for employment in more extra than one field.

Conclusion

In the current study, we explained the potential of *Marrubium vulgare* L. leaves water-ethanolic extract for the inhibition of the corrosion of metals (Iron, Copper and Aluminium) in aqueous solutions, including phytochemicals- physicochemical analysis and antibacterial activity. The results from this extract was a good inhibitor for selected metals corrosion, also is positively toward existing of phytochemicals, qualitatively and quantitatively analyzed, physicochemical parameters, hydrogen-producing As an obtained results, that the crude extract of an extract of *Marrubium vulgare* L acts as a mixed-type inhibitor and may aid as an active corrosion inhibitor of metals in aqueous solution. From the acquired results of antibacterial, the examination exhibited that the crude extract of leaves was very effective against all types of bacteria *Escherichia Coli, Klebsiella pneumonia, Proteus Vulgaris* and *Staphylococcus aureus.*

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Conflict of Interest

The authors declare that no conflict of interest exists.

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