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Corrosion Inhibition of carbon steel XC70 in two acidic media (0.1 N H_2SO_4) and (0.1 N HCl) by weight loss method using Black Pepper Extract as corrosion inhibitor

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Abstract

Black pepper (*Piper Nigrum* L.) extract and ecologically friendly inhibitor were employed in this investigation. According to the data, the corrosion rate in the hydrochloric acid medium (HCI) is greater than the corrosion–rate in the sulfuric acid (H_2SO_4) medium. The corrosion rate of carbon steel varies depending on the corrosion medium. With an increase in inhibitor concentration, the percentage of inhibition increases. By using electron impact mass spectrometry, the mass fragmentation routes of several piperines from black pepper (*Piper Nigrum* L.) were examined (EI-MS). Different intensities of the molecular ion peaks M^{+2} and M^{+} were captured. By successively losing simple functional groups, followed by the breakdown of the heterocycles attached to the pyrimidine ring, distinctive fragment ions were created.

Keywords: Mass spectrometry, Fragmentation processes, Corrosion inhibition, Piperine, *Piper Nigrum L.*

Introduction

The family Piperaceae includes the naturally occurring chemical substance known as piperine (*1*). A nitrogenous, pungent compound known as piperine is an alkaloid that is present (*1*). Antidepressant, hepatoprotective, antioxidant, anticancer, antibacterial and antispasmodic properties are all present in piperine's fruit (*2*).

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Additionally, piperine has the power to lower inflammation, relieve pain, enhance digestion, and boost bioavailability (*3*). Additionally, piperine is capable of improving bioavailability, increasing digestion and reducing discomfort (*4*). An alkaloid called piperine is present in about 98% of water chestnuts that come from plant sources are pure (*5*). Since piperine is known to be these plants' primary alkaloid. In order to create the pungency of black and long pepper, the natural alkaloid piperine and its isomer chavicine are utilized as bio-enhancers (*6*) . One of the best ways to prevent corrosion of metals is to use corrosion inhibitors. By adsorbing ions or molecules on the metal surface, inhibitors slow the rate of corrosion (*7*). The majority of corrosion inhibitors are synthetic compounds, which cost a lot of money and have adverse effect for the environment. Finding environmentally friendly inhibitors that outperform traditional solutions in terms of cost-effectiveness, performance, and adaptability is thus necessary (*8, 9*). An intriguing group of sources for the compounds that are now exported for the majority of systems to prevent metal corrosion from occurring are plants. The current study was soughed to determine the inhibitory effects of black pepper extract on corrosion using the mass loss method.

Materials and Methods

All melting factors had been measured on a Gallen Kamp electric melting factor equipment and are uncorrected. IR spectra had been recorded the use of KBr discs on a Pye Unicam SP-3-300 infrared spectrophotometer. The mass spectra had been recorded on a Shimadzu GCMS-QP-1000EX mass spectrometer at 70 eV. All the spectral measurements had been done on the Microanalytical Centre of Cairo University, Egypt.

Plant Material

Black pepper (*Piper nigrum* L.) seeds were collected from the market of Tripoli, Libya. It is based on powder and then keep a dry container. All chemicals obtained from the Faculty of Science Laboratory, Department of Chemistry, University of Tripoli. The work was carried out in the organic chemistry laboratory.

Isolation of piperine

Black pepper dried fruit was used to isolate piperine. 100 mL of analytical grade ethanol was used to extract 30 g of ground fruit over the course of 120 minutes. The solution was concentrated in a vacuum-sealed evaporative bath with a 10 mL. Cold solution with constant stirring, 10% alcoholic potassium hydroxide was added to the filtrate. The insoluble residue was then filtered, and the alcoholic solution was then left overnight with a few drops of water, causing a yellow solid to precipitate. This led to extensive washing with diethyl ether followed by recrystallization with ethanol, which produced yellowish crystals that were identified as piperine by comparing the results of spectroscopic (FTIR and MS), physical data (mp=126-127°C) measurements and chemical tests. All alkaloid tests were positive, showing blood red, especially concentrated sulfuric acid. A reddish-brown precipitate was obtained with Dragendroff's reagent (*10*).

Preparation of *Piper longum* Fruit Extract

Piper longum fruit was dried and ground to powder form. Dried (10 g) powder was soaked in double distilled water (500 mL) and refluxed for 5 h. The aqueous solution was filtered and concentrated to 100 mL. This extract was used to study the corrosion inhibition properties.

Steel used: Experiments were carried out on samples of XC70 carbon steel, which were mechanically cut by cold cutting (*11*). They are shown in the following Table.

Table 1: Elemental percentages of the XC70 steel used

The ingredients	C	Si	Mn	P	S	Cr	Mo
Wt.%	0.005	0.245	1.685	0.002	0.001	0.042	0.005
The ingredients	Fe	V	Ti	Nb	Cu	Al	Ni
Wt.%	97.77	0.014	0.19	0.067	0.010	0.042	0.026

Preparation of the corrosive medium (electrolyte solution):

Corrosion occurs on the basis of the interactions that occur between the metal and the surrounding medium, and for this we have studied the effect of the behavior of carbon steel XC70 in two acidic media (H_2SO_4) and (HCl). The electrolyte solution (0.1N H_2SO_4) and (0.1N HCl) was prepared using distilled water to avoid the influence of ions such as chlorine ions.

Preparation of the inhibitory (mother solution)

A mass of 100 g of dry plant was soaked in a volume of distilled water for 24 hours at laboratory temperature, after which it was filtered (the process was repeated three times, that is, it was filtered after every 24 hours and then distilled water was added each time after filtration for 3 days). The filtrate was collected and the filtration process was repeated several times to obtain the mother solution, from which we prepared it. The study solutions were also determined in volumetric and mass concentrations of the aqueous extract (*12*) (13). After the soaking process, the filtrate, which is a vegetable powder, was taken and left to dry.

Experimental study of the solvent Methods used Mass loss method

Principle: This method depends on the change in the weight of the sample, so that the sample is weighed before and after it is dipped in aqueous electrolysis solution (*13*).

Materials used: The most important materials used in this study presents: Sulfuric acid (96-98%), Hydrochloric acid (35-37 %), Acetone, Distilled Water, Carbon steel.

Sample preparation: The surface of the sample is prepared before it is dipped into the electrolyte solution according to the mechanical polishing process and this depends on the target to be studied, as the surface condition is closely related to the compounds used.

Mechanical Polishing:

The used carbon steel is prepared through the following steps:

- Cutting the sample under cold conditions.
- Choosing the appropriate shape according to the used method of “rectangular prism in this way” until a mirror-like surface is obtained.
- During the polishing process, distilled water is poured onto the sandpaper to get rid of the heat radiating from the metal.
- The sample is washed with distilled water, then dried, then wiped with cotton and moistened with acetone to clean it well and remove the greasy substances sticking to it from the hands or from the work area surrounding it. Steel samples are polished with abrasive papers graded from lowest to

highest number: 80-1500-1200-1000-2000-1000-600-400-200-180-120-200.

Method of work:

In the absence of an impediment:

The weight and area of the samples were taken before immersing it in the acidic solution, then dip it in 40 ml of the acidic solution, and after a certain period of time, the sample is removed from the solution and dipped again in distilled water for a few moments, allowed to dry and then weighed again to determine the amount of mass loss.

In the presence of the inhibitor

The same previous process was repeated, but with the addition of the inhibitor to the medium in bulk concentrations.

Determining the equilibrium time of the XC70 steel using the method of reducing the weight in the two media HCI: H_2SO_4 (0.1N) 9 (0.1N)

To determine the time of the experiment based on it, we conducted the experiment and repeated it several times starting with minutes and hours, so half an hour was chosen for immersion, because at this time a significant erosion of the sample occurred by comparing the experiments conducted at different times shown in each of the two Tables (2 and 3).

Results and Discussion

IR spectra

As shown in Figure 1.; peaks exist for all bonds in piperine crystals isolated nearby Standard IR value of each functional group 3011 (arom. C-H st.), 2914, 2849 (aliph. C-H st.), 1735 (-CO-N-), 1558, 1484 (arom. C=C st.), 1417 (methylenedioxy CH_2 bending), 1254, 1175 (=C-O-C asym. st.), 1037 (=C-O-C sym. st.), 9958 (C-H bending of *trans* –CH=CH-).

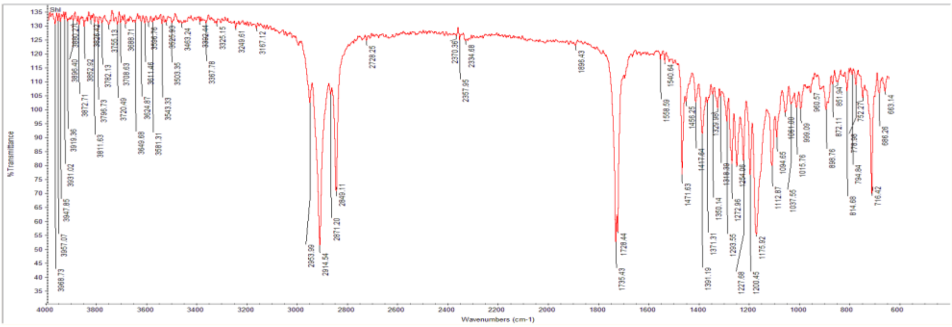

Figure 1: IR spectra of piperine

MS Measurements

The electron ionization mass spectra were recorded on Shimadzu GCMS-QP-1000EX mass spectrometers at 70 eV in Micro analytical center at Cairo University, Giza, Egypt. The electron ionization ion source was kept at 200 ºC. The compounds were introduced with a probe which was ballistically heated to 250 ºC. The EI mass spectra were obtained over the range of *m/z* 50-650.

Piperine mass fragments:

Possible systems of primary mass spectral fragments of piperines. Proposed systems of mass spectral fragments 28-30 of the isomers determined the subsequent mass spectra fragments M+ m/z for piperine: 285.1 ($C_{17}H_{19}NO_3$). Although the fragment of mass 201.0 ($C_{12}H_9O_3^+$) should be shaped with the aid of using the indicated cleavage of the carboxyamide moiety, the mechanisms of formation of the systems with loads of 171.0 ($C_{11}H_7O_2$+) and 143.0 ($C_{10}H_7O^+$). Figure 2 suggests proposed systems of mass spectral fragments 28-30 of the isomers determined the subsequent mass spectra fragments M+ m/z for piperine: 285.1 ($C_{17}H_{19}NO_3$). Although the fragment of mass 201.0 ($C_{12}H_9O_3^+$) should be shaped with the aid of using the indicated cleavage of the carboxyamide moiety, the mechanisms of formation of the systems with loads of 171.0 ($C_{11}H_7O_2^+$) and 143.0 ($C_{10}H_7O^+$).

The structure of piperdine was confirmed by various spectral analyses as mentioned in experimental section. The IR spectrum of the compound gave characteristic absorption band at v_{max} 1735 cm^{-1}, which indicated the presence of an amide carbonyl group. The positive ion FAB MS spectroscopy revealed the presence of protonated molecular ion $[M+1]^+$ peak at 286.2. The FAB+ MS, ^1H spectral analysis of the compound led to establish the molecular formula of the isolated compound as 1-[5-(1,3benzodioxol-5-yl)-1-oxo-2,4-

pentadienyl]piperidine($C_{17}H_{19}NO_3$), which was further confirmed by comparing with published spectral data of the alkaloid pipreine.

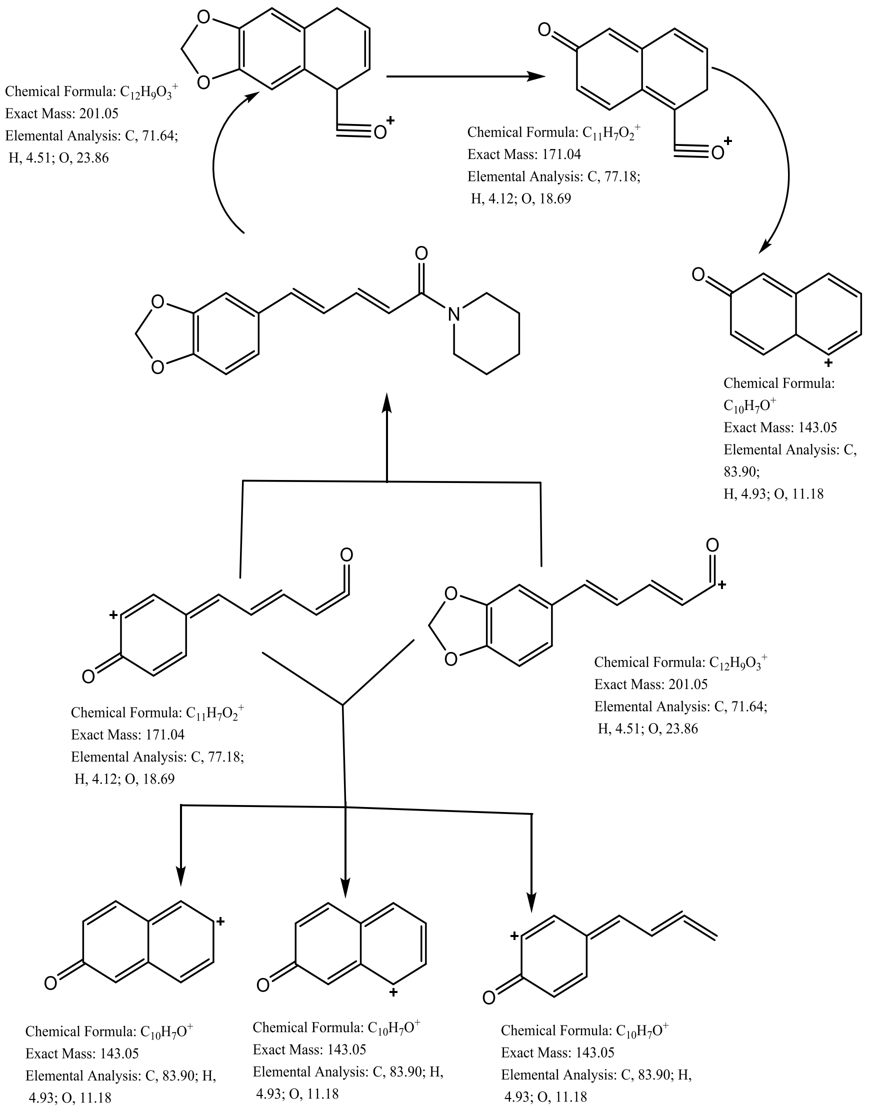

Figure 2: Proposed structures of mass spectral fragments.

Results obtained according to the mass loss method:

In the absence of an inhibitor:

Table 2: Changes in the corrosion rate of XC70 steel as function of time in the absence of an inhibitor in acidic media (0.1 N H_2SO_4)

T (min)	Δm (g)	S (cm^2)	V.10^{6-} (g/cm^2.min)	V (mm/an)	V (µm/an)
10	0.00016	15.8319	0.7421	0.4873	493.9
30	0.00063	15.9107	1.0961	0.7725	761.5
60	0.00085	15.9176	1.0096	0.6831	679.8
90	0.0012	15.8634	1.0086	0.6876	677.2

Table 3: Changes in the corrosion rate of XC70 steel as function of time in the absence of an inhibitor in acidic media (0.1 N HCl)

T (min)	Δm (g)	S(cm^2)	V.10^{6-} (g/cm^2.min)	V (mm/an)	V (µm/an)
10	0.000190	12.89273	0.9980	0.5814	578.6
30	0.000452	12.87361	1.1583	0.8061	805.8
60	0.000676	12.88271	0.89024	0.5988	599.5
90	0.001266	12.89032	0.88703	0.5981	597.1

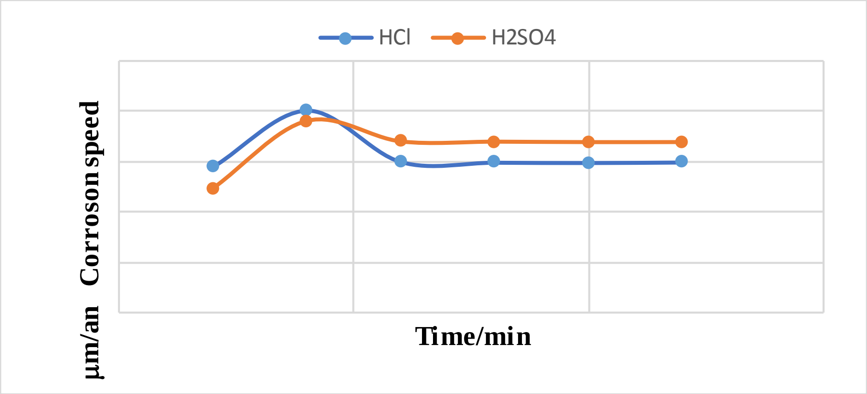

Figure 3: Corrosion rate curve of 70 XC steel as a function of time in the absence of the inhibitor in two acidic media (0.1 N H_2SO_4) (0.1 N HCl) by weight loss method.

In the presence of the inhibitor:

Table 4: Changes in the corrosion rate of XC70 steel in terms of concentration in the presence of the inhibitor in acidic media (0.1 N H_2SO_4)

Concentration volumetric (%)	**Δm (g)**	**S (cm^2)**	**V.10^{6-} (g/cm^2.min)**	**V (mm/an)**	**V (m/an)µ**	**□**	**R (%)**
0	0.0005	15.925	1.130	0.761	761.7	00	00
2	0.00029	12.881	0.6048	0.4073	407.6	0.41	41.90
4	0.00023	12.881	0.4758	0.3208	320.5	0.54	54.30
6	0.00015	12.881	0.3081	0.2077	207.8	0.70	70.38
8	0.00012	12.881	0.2842	0.1425	142.3	0.81	81.30
10	0.00013	12.881	0.3117	0.1603	160.2	0.77	77.16

Table 5: Changes in the corrosion rate of XC70 steel in terms of concentration In the presence of the inhibitor in acidic media (0.1 N HCl)

Concentration volumetric (%)	Δm (g)	S (cm^2)	V.10^{6-} (g/cm^2. min)	V (mm/an)	V (m/an)µ	□	R (%)
0	0.0004	12.881	1.195	0.806	805.8	00	00
2	0.0002	12.882	0.599	0.404	403.8	0.486	48.64
4	0.0001	12.882	0.348	0.235	234.7	0.702	70.15

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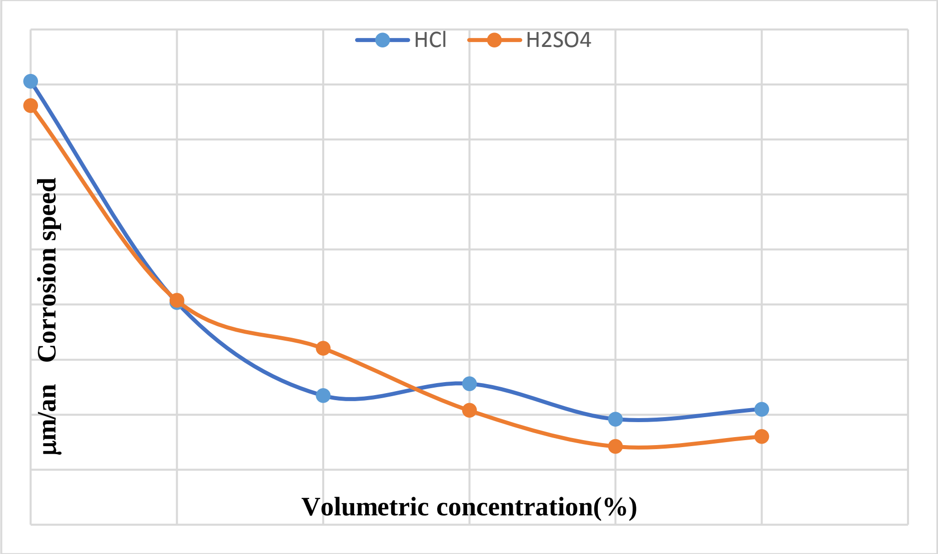

Figure 4: Corrosion rate curve of XC70 steel in terms of concentration in the presence of the inhibitor in acidic media (0.1 N H_2SO_4) (0.1 N HCl) by mass loss method

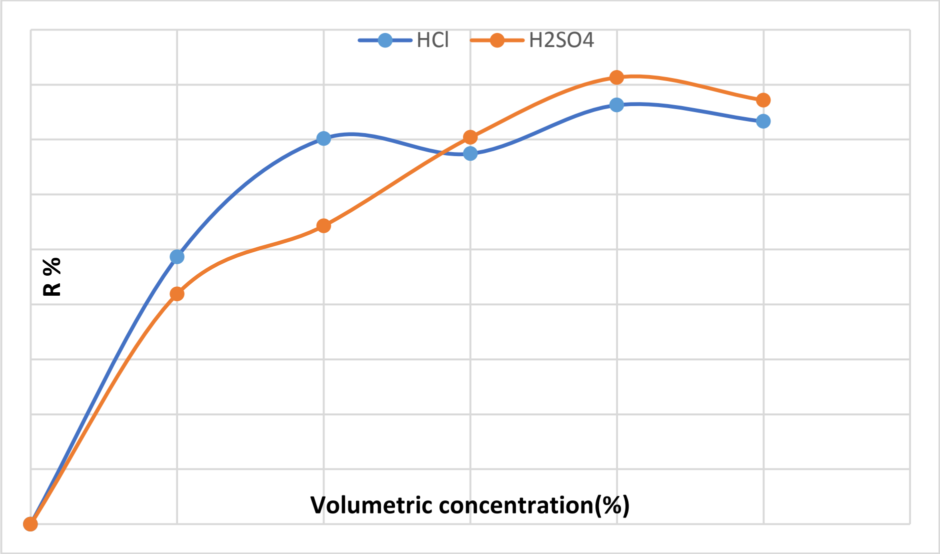

Figure 5: Corrosion rate curve of XC70 steel in terms of concentration In the presence of the inhibitor in acidic media (0.1 N H_2SO_4) (0.1 N HCl) by mass loss method.

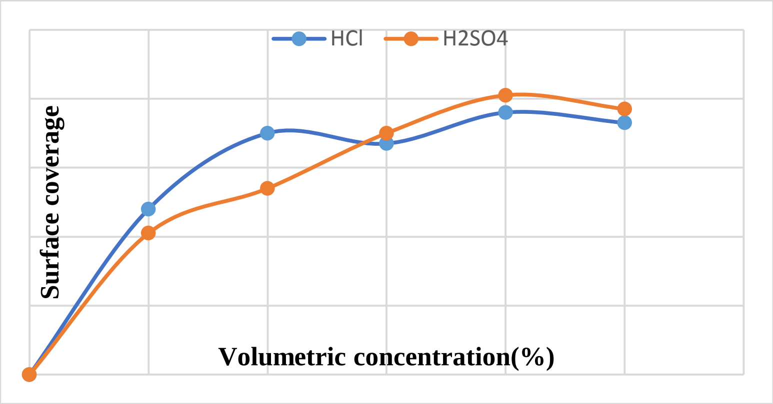

Figure 6: Curve of changes in the ratio of the surface coverage of the inhibitor in terms of concentration in the two acidic media (0.1 H_2SO_4, N)

In the absence of an inhibitor

Through Tables (2 and 3) and the curves, we can clearly observe how the corrosion rate for the two acids changes over time in the absence of the inhibitor (Fig. 3). We observe that the corrosion rate reaches its maximum after 30 minutes and then starts to slow down over time. We find that the corrosion rate of HCl acid (805.7µm/an) is higher than that of H_2SO_4 (761.6µm/an) when comparing the two acids, which causes the corrosion to proceed at its fastest rate, after which the metal activity declines due to the slow rate of the electrochemical reaction with the extension of the exposure time as a result of the buildup of corrosion residues on the surface of the used carbon steel, which prevents the electrochemical corrosion process from continuing. Due to the formation of a protective natural layer, this phenomena sometimes referred to as the quenching phenomenon.

In the presence of the inhibitor

As can be seen from the results obtained and displayed in each of the two Tables (4 and 5), the aqueous extract inhibitor demonstrated modest effectiveness in inhibition at low concentrations, but this percentage increases with increasing concentration. For instance, at a concentration of 2% in the medium of H_2SO_4 (the yield was estimated at 48.64% and the rate value is 403.8µm/an, bringing the yield to 76.28%, while the rate decreases to 142.3µm/an for medium HCl at a concentration of 2%. to 76.280 at a concentration of 8%, after which it begins to decrease in the two acidic mediums.

Figures (3,4 and 5) were shown a direct relationship between inhibitor concentration and inhibition efficacy, with inhibition effectiveness increasing in direct proportion to a reduction in corrosion rate. On the other hand, data shown a rise in the surface 6 coverage ratio, which peaked at 0.81 in the H_2SO_4 media and 0.76 in the HCl medium and coincided with drop in corrosion rate and an increase in concentration ratio. The formation of a yellow layer on the metal's surface, which indicates the formation of a homogeneous surface, can be used to explain these results. As a result, the covered areas become cathodic areas and the other areas become anodic areas, which causes the corrosion rate to increase once more and the percentage to decrease. It is evident from the data displayed in the preceding tables and figures that the percentage of inhibition rises as the extract's concentration in the acidic medium for the two acids utilized increases, reaching its maximum value at an extract concentration of 8%, or (77.402) in the medium. HCl whereas H_2SO_4 (86.375%) is the medium. The inhibitor covering a large portion of the surface, forming a protective layer that prevents the corrosion process, and at the same concentration, the corrosion current reached its lowest value in both media. The same thing we touch in the value of the corrosion rate, due to the existence of a direct relationship between it and the current I (f.v), either the equilibrium potential was equal to (-542.7mv in HCl medium), and (-534.6mv in H_2SO_4 medium).

Thus the corrosion rate in the medium HCl reached a value of (825.3 um/an) in the absence of the inhibitor, which is the greatest compared to the medium H_2SO_4, as it achieved (771.4 um/an). It should be noted that the extract exhibits more inhibition at an 8% concentration in the media H_2SO_4 than it does in the medium HCl. The same is also evident at all concentrations. Results conclude that the corrosive medium, the intensity, and the nature of its action all influence how the corrosion rate, inhibition yield, and behavior change.

Conclusion

It was reached by examining the black pepper (*Piper Nigrum* L.) aqueous extract's ability to suppress corrosion on the carbon steel sample XC70 in corrosive acid media represented by 0.1 N sulfuric acid and 0.1 N hydrochloric acid, respectively. The plant was soaked in distilled water to produce this aqueous extract. The filter was collected after this procedure was carried out three times. The plant's high concentration of the majority of the active ingredients, as revealed by preliminary tests, is what convinced us of its high efficacy. The mass loss method was used as a first way to study the inhibitory effect of this aqueous extract, where the corrosion rate was assessed in the absence and presence of volume concentrations ranging from 2% to 10%. The yield of inhibition was determined. As a result of the findings, it can conclude that phytochemistry can be used to prevent corrosion or at least to reduce it. This is because these natural resources are abundant in active compounds that can adhere to metal surfaces and shield them.

Acknowledgements:

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تثبيط تآكل الفولاذ الكربوني XC70 في وسطين حامضيين (حمض كبريتيك 0.1 عياري) و (حمض هيدروكلوريك 0.1 عياري) بطريقة إنقاص الوزن باستخدام مستخلص الفلفل الأسود كمثبط للتآكل

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المستخلص العربي

تم استخدام مستخلص الفلفل الأسود (*Piper Nigrum* L.) وهو مثبط صديق للبيئة في هذا البحث. وفقًا للبيانات ، فإن معدل التآكل في وسط HCl أكبر من معدل التآكل في وسط H_2SO_4. يختلف معدل تآكل الفولاذ الكربوني اعتمادًا على وسط التآكل. مع زيادة تركيز المثبط ، تزداد نسبة التثبيط. باستخدام مقياس الطيف الكتلي للصدمات الإلكترونية ، تم فحص طرق التجزئة الجماعية للعديد من البيبيرين من الفلفل الأسود (Piper Nigrum L.) (EI-MS). تم التقاط شدة مختلفة لقمم الأيونات الجزيئية M^{+2} و M^{+} من خلال الخسارة المتتالية لمجموعات وظيفية بسيطة ، متبوعة بانهيار الدورات غير المتجانسة المرتبطة بحلقة بيريميدين ، تم إنشاء أيونات شظية مميزة.

الكلمات المفتاحية: قياس الطيف الكتلي ، عمليات التجزئة ، منع التآكل ، مستخلص الفلفل الأسود.