



Comparison of different concentrations efficiency of Artemisia and Sesamum plants extractors as corrosion inhibitors for medium steel specimens in 0.5M HCl at temperature of 25°C

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ABSTRACT

Corrosion of steel is the major problem in building, petroleum pipelines, or plants, so use of protection techniques is most important to reduce metal degradation or plant stopped due to failure of machines that lead to increase of maintenance or replace part damaged cost. The purpose of this study is to investigate the effect of an inhibitor on the corrosion inhibition potential of mild steel using organic inhibitors from Artemisia and Sesamum plant extracts. The study was carried out using the weight loss technique. Using different concentrations of plant extracts from each type at 25 °C and measuring the weight of medium steel (MS) samples before and after immersion in the media of HCl acid and inhibitor. The results obtained showed that the inhibition efficiency of the extract increases with an increase in the concentration of the extract. The adsorption isotherm of natural product on the steel has been determined.

مقارنة كفاءة التركيز المختلفة لمستخلصات نبات الشيح والسوسم كمثبطات تأكل لعينات الحديد متوسط الكربون في 0.5 مول من حمض الهيدروكلوريك عند درجة حرارة 25°م

معمر خليفة و مسعودة فرحات و موسي مي و طه عبدالله

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الكلمات المفتاحية:

حديد متوسط الكربون
المثبط
مستخلص
معدل التآكل
محلول حمض الهيدروكلوريك

الملخص

تآكل الحديد في البناء وأنابيب نقل النفط أو المصانع من المشاكل الكبيرة، لذلك استخدام تقنيات الحماية مهمة جدا لتقليل فقد المعدن أو توقف المعدن نتيجة لانهيار المعدات وبدوره تؤدي إلى زيادة تكلفة الصيانة أو استبدال الجزء المتضرر. الغرض من هذه الدراسة هو دراسة تأثير المانع على قدرة تثبيط التآكل للفولاذ الطري باستخدام مثبطات عضوية من مستخلصات نبات الشيح والسوسم. أجريت الدراسة باستخدام تقنية فقدان الوزن. تم استخدام تراكيز مختلفة من المستخلصات النباتية من كل نوع عند درجة حرارة 25م وقياس وزن العينات الفولاذية المتوسطة قبل وبعد غمرها في وسط حامض HCl والمثبط، وأظهرت النتائج المتحصل عليها أن كفاءة التثبيط للمستخلص تزداد بزيادة التركيز المستخلص. تم تحديد تساوي درجة حرارة الامتزاز للناتج الطبيعي على الحديد متوسط الكربون.

Introduction

Corrosion occurs when pure metals and alloy react chemically or electrochemically with the corrosive environment such salt solution to form insoluble corrosion product. Corrosion mechanism includes the passage of electrons from the anode (more active metal) to the cathode (less active metals) this process is known as the charge transfer process, at the cathode electrons accepted by oxygen, hydrogen ions or oxidizing agents [1,2,3,4,5,6]. Medium Steel (MS) is used most widely in industrial applications such as petrochemical production systems, also used in the manufacture of oil pipes, power plants, tanks, etc. although it is more resistant to corrosion in aggressive environments, however demands protected to extend its

existence [7]. To cleaning and remove unwanted scales and corrosion dust from the metal surface many acids are used for this purpose for example HCL, H₂SO₄, and H₃PO₄. But these acids are corrosive agents which may cause damage to the metal and thus reduce its lifetime [8], for this many researchers and scientists seek to discover reasonable solutions to retard its corrosion and give ideal protection that can extend its lifetime [9]. To minimize corrosion rate of metals, there are several ways used such as cathodic protection, anodic protection, coating, Alloying and recently been used laser for the same purpose to improve some properties of metals such as roughness, hardness, resistance to corrosion by surface treatment of

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metal, etc. [10,11]. There is another way to reduce dissolution or loss of metals by adding corrosion inhibitors, where corrosion inhibitors are the chemical compound that reduce corrosion rate of metals when being added to the liquid or gas that the metal is in contact with. [12]. Researchers reported using phytochemical as corrosion inhibitors, in the 1972, the aqueous extract of Hibiscus subdariffa (karkade) by El hosary and his team [13] as an inhibitor in acidic and alkaline medium. Also nicotine [14] and caffeine [15] used as effective corrosion inhibitor for MS in neutral environment was explained by Srivastava and Sanyal. Tobacco, black pepper, castor oil seeds and lignin are also used as inhibitors for MS corrosion in an acidic solution and they tacked high degree of corrosion control in acidic solution and was done by Srivastava and Srivastava [16]. In order to produce safe inhibitors, research is currently focused on plant extracts since they are eco-friendly, easily accessible, affordable, and renewable sources of efficient corrosion inhibitors [17–23]. Plant extracts with nitrogen, oxygen, or sulphur atoms have been utilized to prevent the corrosion of zinc and other metals in solutions like HCl and NaCl [24–28]. In this study we will use Artemisia & Sesamum extractors as natural organic inhibitors. In general, organic inhibitors are most widely used to inhibit corrosion of metals in industry because of their effectiveness at different temperatures, good solubility, and relatively low toxicity [24,25].

2. Materials and Methods

2.1. Chemical compositions of Medium Steel Used in this Work.

The Medium steel test sample that was used for the experiment was found from steel market in Sebha had a compositional specification (in wt %) as follows 95.0% Fe, 0.45C, 1.30% Si, 0.911% Mn, 0.111% P, 0.256% S, 0.334% Cr, 0.0202% Ni, 0.491% Cu, and 0.641% Al as determined by the chemical analysis.

2.2. Preparation of Sesamum indicum and Artemisia leaves:

Aqueous extracts of Sesamum indicum and Artemisia leaves are used to prepare a stock solution of the plant's leaves: In a round bottom flask with an air condenser, 20 g of dried and ground Sesamum indicum and Artemisia leaves powder was heated for 24 hours at 70°C with 500 ml of distilled water. After being allowed to stand overnight, the extract was filtered and made up to 500 ml with distilled water.

2.3. Corrosion Measurements

A weight loss approach was used to calculate the rates of corrosion for steel samples that were inhibited and uninhibited. At 25°C, weight loss measures were taken. These cylinders were submerged in 0.5M HCl, and the loss weight of each successive weighting sample exposed to the test solution for rinsed, dried, and weighted w_2 was noted. According to weight loss in gm. $\text{cm}^{-2}\text{min}^{-1}$, the corrosion rate of weight loss (CR) was determined using Equ. (1):

$$CR = \frac{w_2 - w_1}{A \cdot t} \quad (1) \quad [29]$$

Where w_1 and w_2 are the corrosion rate of the mild steel specimen in the absence and presence of inhibitor, respectively, A is the surface area of mild steel specimen and t is the time of each exposure. The percentage of inhibition efficiency (I. E) of a corrosion inhibitor is calculated from the corrosion rate values using Equ. (2).

$$I. E = \left[1 - \frac{CR_{\text{Corr. add}}}{CR_{\text{Corr. free}}} \right] 100 \quad (2) \quad [30]$$

Where, $CR_{\text{corr., free}}$ and $CR_{\text{corr., add}}$ are the corrosion rates in the absence and presence of a certain concentration of the inhibitor.

3. Results

3.1. Corrosion Rate (CR):

The relationship of specimens and inhibitor concentration of the current study are presented in figure (1) for Artemisia extracts and sesamum indicum aqueous extract, at temperatures of 25°C.

According to figure 1 the corrosion rate in Artemisia and Sesamum indicum extracts is inversely correlated with the inhibitor concentration, which means that when the inhibitor concentration increases the corrosion rate decreases. According to some researchers, a metal rate of corrosion doubles for every 10°C [31], as the concentration of the extract in solution is raised, the results demonstrate a continuous increase in the efficiency of inhibitor [32]. The corrosion rate decreases, and the efficiency of the inhibitor increases, which indicates that the inhibitor molecules are adsorbed

and provide a barrier on the metal surface [33]. These outcomes demonstrate that both extracts have a respectable level of corrosion-inhibiting potential.

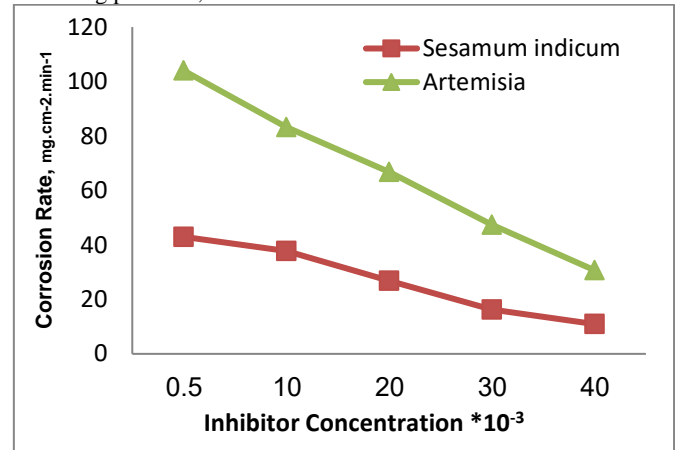


Fig1. Corrosion Rate of Artemisia and Sesamum indicum extracts

3.3. Inhibition Efficiency (IE):

The Inhibition Efficiency (IE %) is presented in figure (2) for both temperatures 25°C. The results show a consistent increase in inhibition efficiency as the concentration of the extract in solution is increased. We found that the values of efficiency and surface area covered increase with increasing concentrations of the used inhibitor. It can be inferred that gradual increase in inhibitor concentration increases the percentage of inhibition efficiency. Hence, when the inhibitor concentration increases, the corrosion rate decreases which directly related to the improves in the adsorption mechanism. A current study showed that the percentage of inhibition efficiency of both sesamum indicum and artemisia leaves increase as the inhibition concentration increases [34–35].

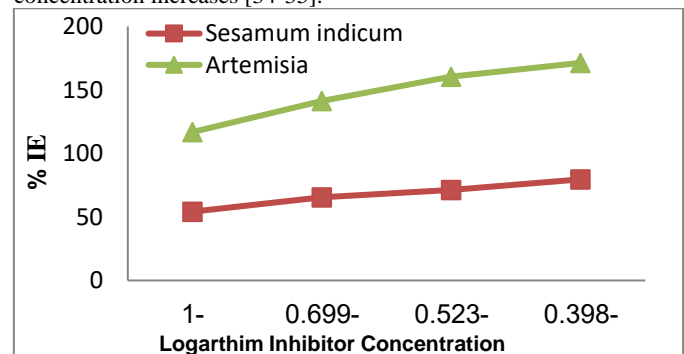


Fig 2. Inhibition Efficiency of Artemisia and Sesamum indicum extracts.

3.3. Adsorption Isotherm:

In general, the adsorption is governed by a number of forces such as covalent bonding, electrostatic attraction, hydrogen bonding, non-polar interactions between the adsorbed species, lateral associative interaction, solvation, and desolvation [36]. The adsorption isotherms define the molecular interactions of the inhibitor molecules with the active sites on the metal surface [37–38].

The isotherms tested were Langmuir, Temkin, Freundlich, the linear regression coefficient of determination (R^2) was used to determine the model that fitted best to the experimental values.

3.3.1. Langmuir Adsorption Isotherm

The Langmuir model assumes that the particles of this is due to the tendency 2 The inhibitor adsorbs in a dense monomolecular layer on the metal surface [39].

Where, K is the adsorption constant, it represents the relationship between surface coverage and the inhibitor concentration. Large K values mean better and stronger interaction between the inhibitor molecules and the metal surface.

A correlation between coverage (θ) defined by (IE %) and the concentration of inhibitor (I) in electrolyte can be represented by the Langmuir adsorption isotherm [40].

$$\theta / (1 - \theta) = K \cdot [I] \quad (3) \quad [40]$$

The value of adsorption constant "K" at each inhibitor concentration were calculated for 25°C as shown on tables (1) and (2). The obtained

values of adsorption constant were used to determine the Gibb's free adsorption energy (ΔG_{ads}), using the following equation [41]:

$$K = 1/55.5 e^{(-\Delta G_{ads}/RT)} \quad (4) \quad [41].$$

Adsorption process on a surface in general, negative values of Gibbs energy indicate ads in ΔG . it can be observed that all values using both temperatures have negative signs, which thermodynamically indicate that the spontaneous adsorption of inhibitor on the surface of low carbon steel was enhanced (indicates the occurrence of exothermic process). The negative value of also suggest the strong interaction of inhibitor molecules with the low carbon steel surface [42].

Langmuir adsorption isotherm was found to be best fit among these four adsorption isotherms, a straight line with ($R^2 = 0.9901$ and $R^2 = 0.9812$) as shown in figure (3).

Table 1: Adsorption Energy of Sesamum indicum extracts at 25 °C

Sample	K	ΔG
0	00	00
10	636.1	-16.044
20	496.6	-15.428
30	429.2	-15.065
40	329.2	-14.406

Table 2: Adsorption Energy of Artemisia extracts at 25 °C

Sample	K	ΔG
0	00	00
10	513.9	-15.594
20	429.1	-15.016
30	332.6	-14.384
40	267.8	-13.849

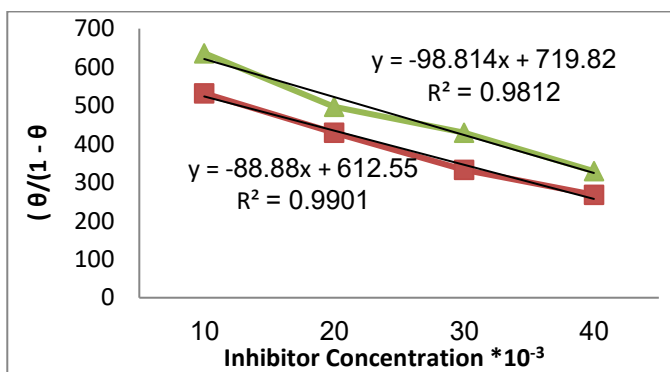


Fig3. Langmuir Adsorption Isotherm of Artemisia and Sesamum indicum extracts

3.3.2. Temkin Adsorption Isotherm:

The Temkin model of isotherm adsorption contains a factor which explicitly takes into account the interactions of ions of the aqueous solution and the membrane (adsorbent - adsorbate). The surface coverage values for "Artemisia and Sesamum indicum extracts" were fitted into the Temkin adsorption isotherm model, which has the form [43]:

$$\text{Exp}(-2a\theta) = K \cdot C \quad (5) \quad [43]$$

K is the equilibrium constant of the inhibitor adsorption process, "a" is the parameter of interaction between inhibitor molecules adsorbed on the steel surface, and θ is the degree of surface coverage, C is the inhibitor concentration.

In figure (4), the obtained values of the correlation " R^2 " for inhibitor temperatures at 25°C of Artemisia and Sesamum indicum extracts were (0.9901) and (0.9812), respectively.

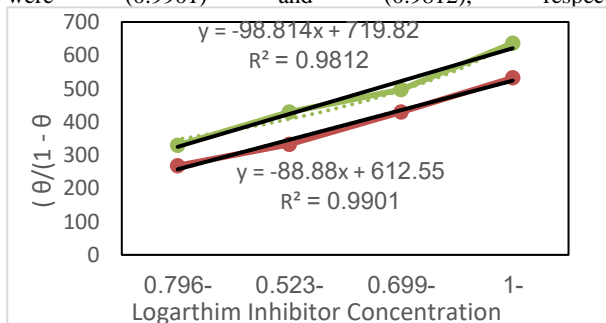


Fig4. Temkin Adsorption Isotherm of Artemisia and Sesamum

indicum extracts

3.3.3. Freundlich Adsorption Isotherm:

The Freundlich model of isotherm adsorption has been chosen fourthly to evaluate adsorption potential of the adsorbent and adsorbed solution. The Freundlich isotherm is given by [44]:

$$\text{Log } \theta = \text{log } K_{ads} + n \text{ log } I \quad (6) \quad [44]$$

Where K_{ads} is the adsorption equilibrium constant, n is the interaction parameter and I is the inhibitor concentration. As shown in the figure (5) a perfectly linear plot was obtained with regression constant (R^2) (0.9516) and (0.873) at temperature of 25°C.

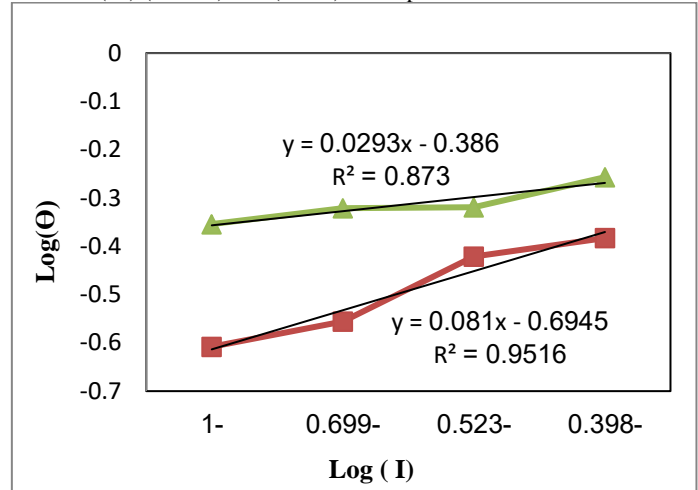


Fig5. Freundlich Adsorption Isotherm of Artemisia and Sesamum indicum extracts

Conclusion

Sesamum indicum and Artemisia leaves are a natural sources of material that can include antioxidants and other organic agents. However, we can extract natural organic inhibitors from them easily, to reduce material degradation for mild steels as an inhibitor in this study. In this work mild steel bar weight reduction was observed, measured, and properly recorded. With increasing concentrations of the leaf extract from Sesamum indicum and Artemisia, it was discovered that the rate of steel bar corrosion in the HCl solution decreased. Clearly was observed that from corrosion rate measurements and inhibitor efficiency, Artemisia extractor reduces corrosion rate more than Sesamum extractor for the same concentration used.

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