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FENUGREEK SEEDS EXTRACT PERFORMANCE AS A GREEN CORROSION INHIBITOR FOR ALPHA-BRASS IN NITRIC ACID SOLUTION

Ghalia A. Gaber[1] and Seham Shahen[1]*

[1]*Department of Chemistry, Faculty of Science (Girls), Al-Azhar University, P.O. Box: 11754, Nasr City, Cairo, Egypt*

* Corresponding author: Seham@azhar.edu.eg

ABSTRACT

In this study, the performance of an aqueous extract of fenugreek seeds (AEFS) as an inhibitor of alpha-brass corrosion immersed in 1 M HNO_3 was investigated by mass loss technique, the results showed that the inhibition efficiency increases to reach 96.48 percent at 10 percent of (AEFS) with increasing concentration. The impact of temperature on alpha-brass corrosion conduct immersed in 1 M HNO_3 without and with the inhibitor was tested in the temperature range of 303 and 343 K at 10 percent of (AEFS). Various adsorption parameters (E_a, G°_{ads}, K_{ads}) show a strong interaction between the inhibitor and the surface of the alpha-brass. The Langmuir adsorption isotherm was obtained by the adsorption of (AEFS) on the alpha brass surface. The surface analysis was performed using an electron microscope scanning technique that confirmed the formation of a protective layer in the presence of the extract on the alloy surface.

Keywords: Fenugreek, Corrosive medium, Weight-loss method, α-Brass, SEM-EDX.

1. INTRODUCTION

Brass, a copper and zinc alloy, is an important and fascinating commodity known for its technical properties and has a wide variety of uses, from mechanical engineering to medical applications and the arts. Some factors cause the alloy to undergo corrosion destruction in each of these areas of brass exploitation, most frequently starting with a selective dissolution of zinc [1-5]. The use of inhibitors is one of the scientifically substantiated and economically expedient methods to protect the brass from corrosion [6]. Organic compounds of higher molecular weight with heteroatoms (with lone electron pairs such as N, S, O) are commonly used as inhibitors. Many organic and inorganic inhibitors are, sadly, poisonous, and non-biodegradable. Owing to the growing understanding of health and the environment, more focus is put today on the use of natural plant products. Plant extracts are organic, containing proteins, poly-carboxylic acids, polysaccharides, tannins, alkaloids, pigments, etc. These compounds function in acidic environments as potential inhibitors for several metals [7-12].

The goal of the present work is to demonstrate the corrosion inhibitory properties of aqueous extract of fenugreek seeds (AEFS) using 1 M HNO_3 alpha-brass weight loss. Various thermodynamic parameters have been calculated and addressed for inhibitor adsorption on the mild steel surface. Kinetic parameters have been tested and interpreted for mild steel corrosion in the absence and presence of the inhibitors tested. Fenugreek seed selection was made because it is herbal medicine and is usually considered healthy.

2. EXPERIMENTAL

2.1. Materials and solutions

Examinations were performed using alpha-brass with the following composition (wt%): Cu 75 % and Zn 25 %. The aggressive solution used was prepared by dilution of analytical reagent grade 67.5% HNO_3 with distilled water. The stock solution (10%) of AEFS was used to prepare the desired concentrations. The concentration range of AEFS used was 2-10 %.

2.2. Preparation of plant extracts

The fresh seeds of Fenugreek were washed under running water, shade dried, powdered and then 10g of powder was soaked in 250 mL of 1 M HNO_3 and boiled for 4 hours. After that solution was left overnight and then filtered and made to 250 mL by 1M HNO_3.

2.3. Weight loss measurements

2.3.1. Effect of concentration of AEFS

Alpha-brass specimens were immersed in 100 mL of the inhibited and uninhibited 1 M HNO_3 solutions. After specified periods, the weight of each specimen before and after immersion was determined using an electronic balance. The inhibition efficiency (IE) and corrosion rate (CR) are determined by:

$$\%IE = (W_2 - W_1 / W_2)\ X100 \qquad (1)$$

Where W_1 and W_2 are the weight reduction of the alpha-brass in the presence and absence of inhibitor, separately.

$$\text{The level of surface coverage } (\theta) = IE/100 \qquad (2)$$

The corrosion rate (CR) was determined from the accompanying condition

$$CR = (\Delta m)/\ (S.t) \qquad (3)$$

where Δm (mg) is the specimen weight before and after immersion in the tested solution, S is the area of the alpha-brass specimen (cm^2) and t is the exposure time (h).

2.3.2. Adsorption isotherm

The type of adsorption isotherm can provide additional information about the properties of the tested compounds. To obtain the adsorption isotherm, the degree of surface coverage (θ) of the inhibitors must be calculated with several adsorption isotherms. In this study, the degree of surface coverage values (θ) for various concentrations of the inhibitor in acidic media has been evaluated from the weight loss measurements.

2.3.3. Effect of temperature

The effect of temperature on the inhibited acid–the metal reaction is very complex, because many changes occur on the metal surface such as rapid etching, desorption of inhibitor and the inhibitor itself may undergo decomposition. The change of the corrosion rate with the temperature was studied in 1 M HNO_3 during 2 h of immersion, both in the absence and presence of inhibitor at a concentration corresponding to the maximum inhibition efficiency. For this purpose, gravimetric experiments were performed at different temperatures (303– 343 K). To calculate activation thermodynamic parameters of the corrosion process, Arrhenius Eq. (4) and transition state Eq. (5) were used [13]:

$$CR = A\exp\left(-\frac{E^{\circ}a}{RT}\right) \qquad (4)$$

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S^{\circ}a}{R}\right)\exp\left(-\frac{\Delta H^{\circ}a}{RT}\right) \qquad (5)$$

where E°a is the apparent activation corrosion energy, R is the universal gas constant, A is the Arrhenius preexponential factor, h is the Plank's constant, N is the Avogadro's number, ΔS°_a is the entropy of activation and ΔH°_a is the enthalpy of activation.

2.4. SEM and EDEX investigation

The morphology of the alpha-brass specimens was examined after exposure to 1 M HNO_3 in the absence and presence of an optimum concentration of the AEFS inhibitor. JEOL 5410 scanning electron microscope SEM (Japan), equipped with an energy dispersive X-ray spectrometer to identify the morphological and chemical information of alpha-brass.

3. RESULTS AND DISCUSSION

3.1. Effect of Inhibitor Concentration

The values of percentage rate inhibition efficiency (IE %) and corrosion rate (CR) got from weight reduction technique at various concentrations of AEFS at 298 K are condensed in Table 1 and Figure 1.

Table 1: Weight loss results of alpha-brass in 1M HNO_3 without and with different concentrations of AEFS at 298 K.

Concentration (%)	Rate of corrosion (CR) (mg cm^{-2} hr^{-1})	Coverage surface (θ)	Efficiency (IE %)
Blank	0.0209	-	-
2	0.0115	0.4473	44.73
4	0.0085	0.5923	59.23
6	0.0054	0.7405	74.05
8	0.0033	0.8374	83.74
10	0.00073	0.96488	96.48

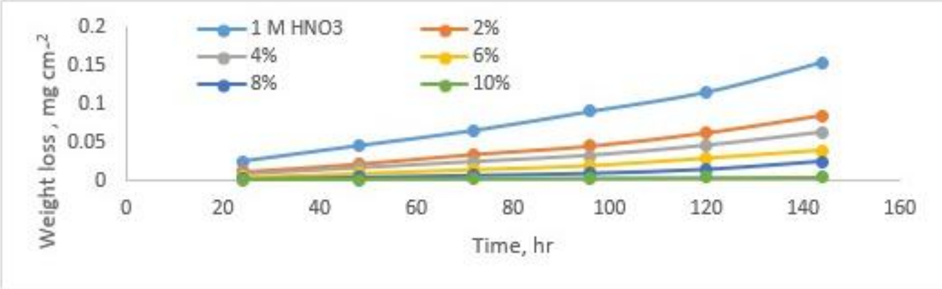


Fig. 1. weight loss-Time curve for the corrosion of alpha-brass in 1M HNO_3 acid solution in the absence and presence of different concentrations of AEFS inhibitor at 298K.

The outcomes got in Table 1 and Figure 1 showed that the corrosion rate (CR) of alpha-brass diminished consistently with expanding the inhibitor concentration, i.e., the consumption of alpha-brass is hindered by AEFS. In any case, the inhibition efficiency IE% increments pointedly with increment in the concentration of inhibitor arriving at a most extreme estimation of 96.48 at 10 %. This conduct could be clarified by the adsorption of phytochemical segments of the AEFS onto the alpha-brass surface bringing about the hindering of the response destinations, and assurance of the alpha-brass surface from the assault of the consumption dynamic particles in the corrosive medium [8]. Thusly, we can infer that the AEFS is a good corrosion inhibitor for alpha-brass in 1 M HNO_3.

3.2. Adsorption isotherm

To characterize the metal/inhibitor/ environment system, the surface coverage values (θ) calculated from the weight reduction technique were tested graphically for fitting a suitable adsorption isotherm and the best fit was found to obey the Langmuir adsorption isotherm [14], which may be expressed by:

$$C/\theta = 1/K_{ads} + C \qquad (6)$$

where C is inhibitor concentration and K_{ads} is the equilibrium constant of the inhibitor adsorption 28.810. Fig. 2 shows the plot of C/θ versus C which is typical of the Langmuir adsorption isotherm. A perfectly linear plot was obtained with regression constant $R^2 = 0.97135$ and slop about unity 0.7294. It is well known that the standard adsorption free energy (ΔG_{ads}), is related to the equilibrium constant of adsorption and can be calculated by the following equation [14]:

$$K_{ads} = 1/55.5 \exp(-(\Delta G_{ads}/RT)) \qquad (7)$$

where ΔG_{ads} is the standard free energy of adsorption, the value 55.5 is the molar concentration of water in solution in mol dm^{-3}, R is the gas constant, and T is the absolute temperature. Using this equation, the standard Gibbs free energy of adsorption of the AEFS inhibitor at 298K was calculated to be -18.2773 kJ mol^{-1}. This quite negative value demonstrates that the AEFS extract adsorption process is spontaneous. Moreover, values of ΔG_{ads} around -20 kJ mol^{-1} or lower are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), while those more negative than -40 kJ mol^{-1} involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [15]. The calculated ΔG_{ads} value is less negative than -20 kJ mol^{-1} indicates that the adsorption mechanism of the investigated AEFS Extract on alpha-brass in 1 M HNO_3 is typical of physisorption. The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that the investigated inhibitor contains many different chemical compounds which some can be adsorbed chemically and other adsorbed physically [16].

3.3. Effect of temperature

The impact of temperature on the corrosion conduct of alpha-brass in 1 M HNO_3 containing AEFS Extract at 10 % is studied in the temperature range 303-343 K utilizing weight reduction estimations at 2 h. The information on corrosion rates (CR) and corresponding efficiency (IE%) collected were introduced in Table 2 and Fig. 3.

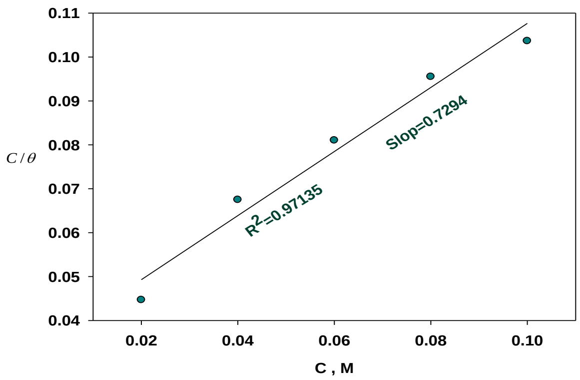


Fig. 2. The plot of C/θ vs. C for the corrosion of alpha-brass in 1M HNO_3 acid solution in the absence and presence of different concentrations of AEFS inhibitor at 298K.

Table 2: Corrosion parameters obtained from weight loss for alpha -brass in 1 M HNO_3 containing 10 % AEFS Extract at different temperatures.

T(K)	CR $_{blank}$ (mg cm^{-2} hr^{-1})	CR $_{inhibitor}$ (mg cm^{-2} hr^{-1})	IE %
303	0.1966	0.00841	95.7
313	0.4424	0.01965	95.6
323	0.8947	0.0550	93.8
333	1.789	0.1240	93.1
343	3.244	0.2440	92.5

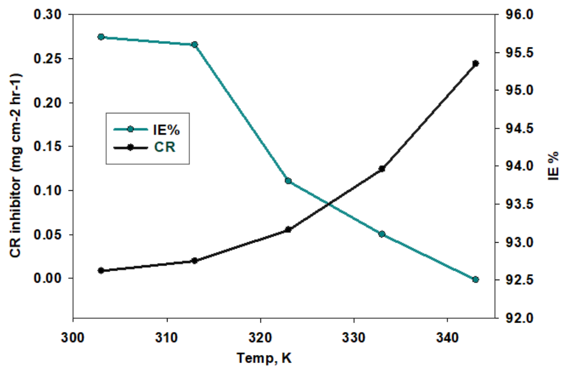


Fig.3. Influence of temperature on corrosion rate (CR $_{inhibitor}$) and inhibition efficiency (IE) of alpha-brass in 1M HNO_3 in the presence of 10% of AEFS Extract at different temperatures.

A review of these outcomes uncovers that the corrosion rate (CR) increments with temperature both in uninhibited and hindered solutions particularly goes up more quickly without inhibitor. This outcome shows that the nearness of the inhibitor prompts the reduction of the corrosion rate. Additionally, we note that the efficiency (IE) relies upon the temperature and diminishes with the ascent of temperature from 303 to 343 K. the efficiency (IE) arrived at high estimation of 95.7 % in 1 M HNO_3 at 303 K, which speaks to the amazing inhibitive capacity of AEFS Extract. The decline in hindrance productivity with increment in temperature might be credited to the expanded desorption of inhibitor particles from the metal surface and the expansion in the solvency of the defensive film or the response items encouraged on the outside of the metal that may somehow or another hinder the response. Fig. 4 represents the plot of ln CR versus (1/T) for alpha-brass in1 M HNO_3 in the absence and presence of 10 % AEFS Extract. Straight lines were obtained with the slope equal to $-E_a/R$. Values of E_a for the corrosion reaction in the absence and presence of AEFS Extract were calculated and are equal to 60.5388, 74.1419 kJ mol^{-1}, respectively. It reveals that the value of activation energy obtained in presence of the inhibited solution is higher than that for an uninhibited solution, suggesting that the dissolution of alpha- brass is slow in the presence of inhibitor due to the formation of a film on the copper surface serving as an energy barrier for the copper corrosion [17]. The apparent enthalpy of activation ΔH_{ads} and entropy of activation ΔS_{ads} values were obtained through the linearized transition – state theory equation 5. Plots of ln (CR/T) versus 1/T for alpha-brass in1M HNO_3 in the absence and presence of 10 % AEFS Extract are shown in Fig. 5, in which straight lines with a slope of ($-\Delta H/R$) and intercept of (ln $(R/Nh)+\Delta S/R$) were obtained the activation enthalpy and the activation entropy. The activation enthalpy in the absence and presence of 10 % AEFS Extract are 57.864 and 71.466 kJ mol^{-1}, respectively. Values of ΔH are positive, which indicates that the corrosion process is endothermic. The activation entropy in the absence and presence of 10 % AEFS Extract are -67.41 and – 49.01 kJ mol^{-1}, respectively. The negative values of ΔS_{ads} in presence of the inhibitor imply that the activated complex in the rate-determining step was association rather than a dissociation step, a decrease in disorderliness took place on going from reactants to the activated complex [18].

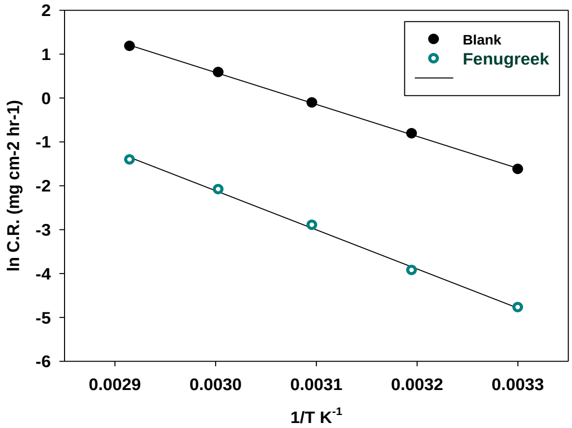


Fig. 4. The plot of ln CR versus (1/T) for alpha brass in1M HNO_3 in the absence and presence of 10 % AEFS Extract.

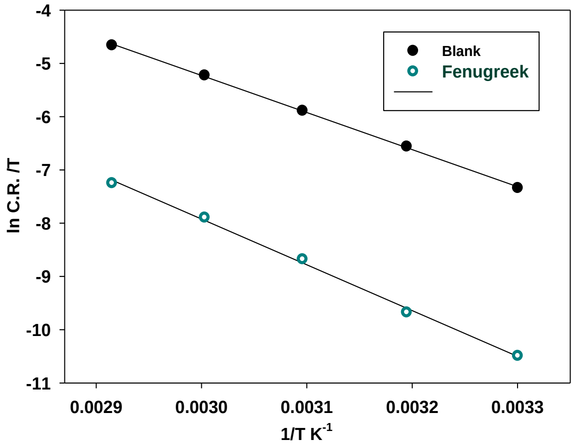


Fig.5 The plot of ln CR/T versus 1/T curves for alpha brass in1M HNO_3 in the absence and presence of 10 % AEFS Extract.

3.4. SEM and EDEX investigation

SEM investigations are conducted to check whether the inhibitor is adsorbed on the surface of the alpha-brass. In Fig.6, the SEM micrograph is shown. In 1 M HNO_3, the alpha-brass surface is found to be seriously affected and there is a pit (Fig.6a). Fig.6 b shows the 10 percent AEFS surface, it is shown that the roughness tends to be reduced with much less corroded area being observed, confirming the AEFS adsorption on the alpha-brass surface active sites, showing a strong inhibiting effect of AEFS.

To analyze the composition of the formed film was studied by EDX as shown in Fig. 7. It is seen that in blank solution EDX shows that the Cu, Zn, and Oxygen are present. In presence of the optimal concentration of inhibitor peak for S, N appeared. Morphology and the EDX of the surface prove that the protective film of AEFS on the alpha-brass surface.

4. Mechanism of inhibition

Ascorbic acid ($C_6H_8O_6$), Beta-carotene ($C_{40}H_{56}$), Xanthophylls ($C_{40}H_{54}$ $(OH)_2$), Choline ($N(CH)_3C_2H_4OH$), and Methionine ($HOOCCHNH_2CH_2CH_2$ SCH_3) are present in many organic substances in fenugreek seeds. It can be found that these substances are organic compounds containing nitrogen, oxygen, and/or Sulphur. It was previously found that through storage and cooking (i.e. boiling), the concentration of ascorbic acid and beta-

(a) (b)

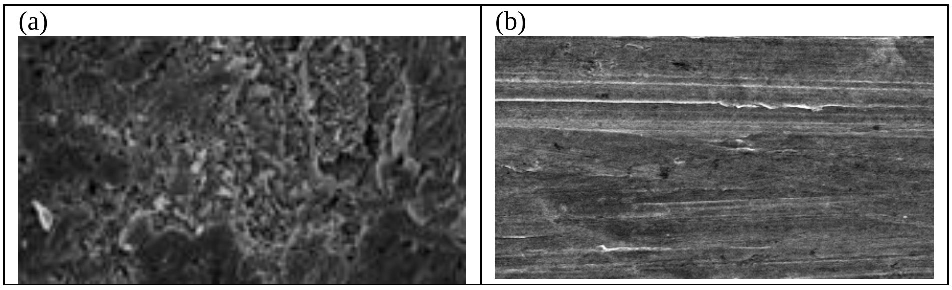
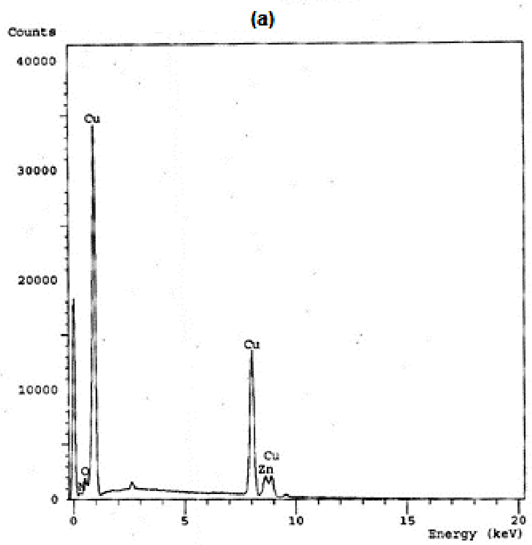


Fig.6. SEM micrographs of alpha-brass surface (a) after 24 h of immersion in 1 M HNO_3 and (b) after 24 h of immersion in 1 M HNO3+ 10% of AEFS.



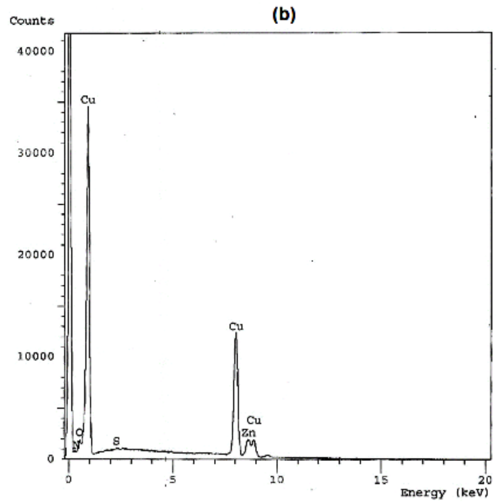


Fig.7. EDX charts of the alpha-brass surface after 24 h immersion in 1 M HNO_3 in the (a) absence and (b) presence of AEFS.

carotene is substantially reduced. Thus, it is not possible to consider these two components as the source of corrosion inhibition. Since Sulphur-containing compounds are not of significant importance in HNO_3 as corrosion inhibitor additives, both choline and methionine compounds in fenugreek leaves can be regarded as the key components in HNO_3 for alpha-brass corrosion inhibition [19].

5. CONCLUSIONS

Extracts of fenugreek seeds were found to be a good, non-toxic, and eco-friendly alpha-brass corrosion inhibitor in 1 M HNO_3. The growing inhibitor concentration decreases metal corrosion and reaches a maximum of 96.48 percent. Langmuir adsorption isotherm is obtained by the inhibitor adsorbed on the alloy surface and forming a protective layer. The creation of a film on the alloy surface has also been supported by SEM pictures.

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فحص أداء مستخلص بذور الحلبة كمثبط لتآكل سبيكة النحاس الأصفر (ألفا) في محلول حمض النيتريك

غالية أسعد و سهام شاهين
قسم الكيمياء - كلية العلوم (بنات)- جامعة الأزهر

الملخص العربي

في هذه الدراسة، تم فحص أداء المستخلص المائي لبذور الحلبة (AEFS) كمثبط لتآكل سبيكة النحاس الأصفر (ألفا) المغمور في $HNO_3$1M بتقنية فقدان الوزن، وأظهرت النتائج أن كفاءة التثبيط تزداد لتصل إلى 96.48٪ عند 10٪. من (AEFS) مع زيادة التركيز. تم اختبار تأثير درجة الحرارة على سلوك التآكل سبيكة النحاس الأصفر (ألفا) المغمور في 1 M من HNO_3 بدون ومع المثبط في نطاق درجة حرارة 303 و343 كلفن عند تركيز 10 بالمائة من (AEFS). تُظهر معاملات الامتزاز المختلفة (E_a و G°_{ads} و K_{ads}) تفاعلًا قويًا بين المثبط وسطح سبيكة النحاس الأصفر (ألفا). تم إجراء تحليل السطح باستخدام تقنية الميكروسكوب الإلكتروني الماسح التي أكدت تكوين طبقة واقية في وجود المستخلص على سطح المعدن.