

Corrosion Inhibition of Muntz (63% Cu, \approx 37% Zn) Alloy in HCl Solution by Some Naturally Occurring Extracts

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Abstract

This work presents the results of corrosion inhibition of muntz alloy (63% Cu, \approx 37% Zn) in 1.0 M HCl by water extracts of some naturally occurring plants. These are: outer brown skin of onion (A), onion bulb (B), the cloves of garlic bulb (C), orange peels (D), and henna leaves (E). The techniques of measurements for the determination of the amount of each zinc and copper dissolved from the alloy in the aggressive solution were: weight-loss, galvanostatic polarization, linear polarization and atomic absorption spectroscopy. From these measurements the values of surface coverage, θ , and inhibition efficiency were calculated. It was found that the investigated extracts have high inhibition efficiency on the corrosion of muntz alloy in 1.0 M HCl. Their inhibition efficiency decreases according to the order: C > D > E > B > A. These extracts behave as mixed inhibitors, i.e., they affect both the cathodic and anodic processes. The activation energy of corrosion was calculated in absence and in presence of extracts. It was found that the presence of extracts in 1.0 M HCl solutions increases the values of activation energy of corrosion in that order of their inhibition efficiency. The inhibiting effect of these extracts results from their adsorption on the electrode surface via the adsorption centers of the compounds present in the extracts. The adsorption of these extracts onto the surface of muntz follows Frumkin's isotherm. The atomic absorption spectroscopic measurements showed that the presence of these extracts greatly inhibits the preferential dissolution of zinc from the alloy and the occurrence of simultaneous dissolution of both zinc and copper.

Keywords: muntz alloy, inhibitors, water extracts, natural products.

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Introduction

The electrochemical behavior of brasses (Cu-Zn) alloys has been extensively studied under different experimental conditions using various measurement methods, including chemical, electrochemical, radiometric, spectro-electrochemical and surface techniques [1-16]. Most of the reported studies are directed to the dezincification process of the different types of brasses [3-10]. When dezincification occurs, regions of the brass become replaced by porous mass of copper, which has no strength nitrogen and / or sulphur heterocyclic compounds as corrosion inhibitors for copper and copper alloys are widely used, and many investigations of the inhibiting mechanism have been carried out [17-26].

The present work aims to investigate the effect of other types of nontoxic compounds such as water extracts of some naturally occurring plants on the corrosion behavior of one of Cu-Zn alloys (muntz alloy) in HCl solution.

Experimental

Muntz alloy, having the composition (63% Cu, \approx 37% Zn), supplied from Alexandria Copper Company, has been used and the measurement techniques were: weight loss, linear polarization and galvanostatic polarization.

For weight loss measurements, the reaction basin used was graduated Pyrex glass vessel with a capacity of 250 mL. In each experiment, 100 mL of the test solution were employed. The investigated metallic specimens were of dimensions $25 \times 25 \times 2$ mm (exposed area of 10 cm^2). The specimens were firstly mechanically polished with emery paper with different grades down to 4/0, degreased with acetone, thoroughly rinsed with bidistilled water, dried with air and weighed. After an exposure-time of two hours the specimen was withdrawn from the reaction solution, rinsed with distilled waters, dried and reweighed. From these weights the corrosion rate R_w ($\text{mg} / \text{cm}^2 \cdot \text{h}$) was calculated. Each experiment was repeated to ensure reproducibility.

For the electrochemical measurements, electrodes of dimensions $15 \times 15 \times 2$ mm were used (exposed area 4 cm^2). Just before the experiments, the electrodes were mechanically polished, degreased and rinsed as above mentioned. A rectangular platinum foil of dimensions 20×20 mm was used as an auxiliary electrode. The potential of the working electrode was measured relatively to a saturated calomel electrode (SCE) as reference. In these measurements the current was derived from a DC power supply, GP- 4303D (LG precision CO- Ltd; Korea) and the potential and current were measured on a digital multimeter, model 1008 (Kyoritsu, Japan). The atomic absorption measurements were carried out by using flam-atomic absorption spectrophotometer (Perkin-Elmer Apparatus Model 23, Germany).

Hydrochloric acid solution was prepared from chemically pure grade (BDH) by appropriate dilution with bidistilled water and standardized.

The inhibitors were water extracts of the following naturally occurring plants:

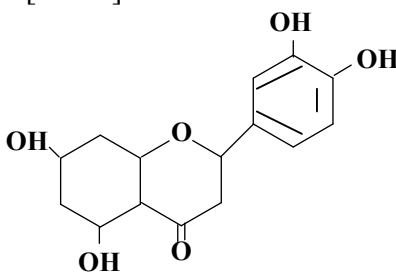
- 1 - outer brown skin of onion "Allium cepa" (A);
- 2 - onion bulb "Allium cepa" (B);
- 3 - the cloves of garlic bulb: "Allium sativum" (C);

- 4 - orange peels “Lawsonia Valencia” citrus sinensis (D);
 5 - henna leaves “Lawsonia inermis” (E).

Preparation of water extracts

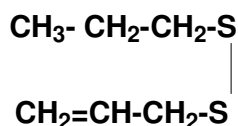
Stock solutions of the extracts were prepared as follows: 10 g of each of outer brown skin of onion (A), henna leaves (E) and 100 g of each of onion bulb (B), the cloves of garlic bulb (C) and orange peels (D) were exhaustively extracted with 200 mL distilled water under reflux for three hours. The solutions were filtered and the resulting extracts were concentrated to 50 mL solution.

The extract of outer brown skin of onion (A) may contain catechol and protocatechuic acid, quercetin (3, 5, 7, 3', 4- pentahydroxy flavone), quercetin-3-glucoside and some tannin [27-29].



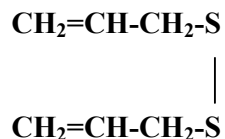
Quercetin

The extract of onion bulb (B) may contain allyl-propyl disulphide ($C_6H_{12}S_2$) in addition to carbohydrates, proteins [30,31].



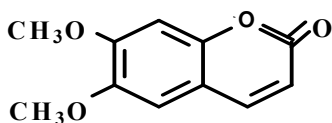
Allyl propyl disulphide

The extract of cloves of garlic bulbs (C) may contain allyl-propyl disulphide, ($C_6H_{12}S_2$), diallyl disulphide, ($C_6H_{10}S_2$), and two more sulphur containing compounds in addition to carbohydrates, proteins [31].



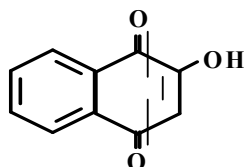
Diallyl disulphide

The extract of orange peels (D) may contain scoparone [32].



Scoparone

The extract of henna leaves (E) may contain the coloring component lawsone (2-hydroxy-1,4-naphthaquinone, C₁₀H₆O₃) [33,34].



Lawsone

Besides lawsone, other constituents present in henna are: gallic acid, glucose, mannitol, fat, resin, mucilage and traces of an alkaloid [31].

The concentration of each inhibitor was calculated taking into consideration the composition of the extract.

Results and discussion

a - Weight loss measurements

The results of weight loss measurements carried out on the alloy in 1.0 M HCl solutions at different temperatures (20, 30, 40, 50 °C) are listed in Table 1. It is clear from these results that the rate of corrosion, R_w , (mg/cm².h) increases with the increase of temperature.

Table 1. Corrosion rates of muntz alloy in 1.0 M HCl at different temperatures.

Temp. / °C	R_w / (mg/cm ² .h)
20	0.50
30	0.60
40	0.75
50	0.90

The weight loss measurements were carried out on the muntz alloy in 1.0 M HCl solution in the presence of different concentrations, M, of the investigated extracts (A, B, C, D, E). The weight loss was determined at the temperature of 20 °C in the presence of different concentrations, while it was determined at different temperatures (20, 30, 40 and 50 °C) in the presence of 2×10^{-6} M of each extract. The different values of inhibition efficiency, I%, were calculated from the rates of corrosion, R_w , by using the following equation:

$$I \% = \left[1 - \frac{(R_w)_{inhi}}{(R_w)_{free}} \right] * 100 \quad (1)$$

where $(R_w)_{free}$, $(R_w)_{inhi}$ are the rates of corrosion ($\text{mg}/\text{cm}^2 \cdot \text{h}$) in the absence and in the presence of the inhibitor, respectively. The calculated values $I \%$ are shown in Fig. 1 for the investigated extracts (A – E). In this figure the inhibition efficiency is represented as a function of temperature for the alloy in 1.0 M HCl solution in the presence of 2×10^{-6} M of each extract. It is clear from the plots of this figure that for a given extract the inhibition efficiency decreases with increasing the temperature.

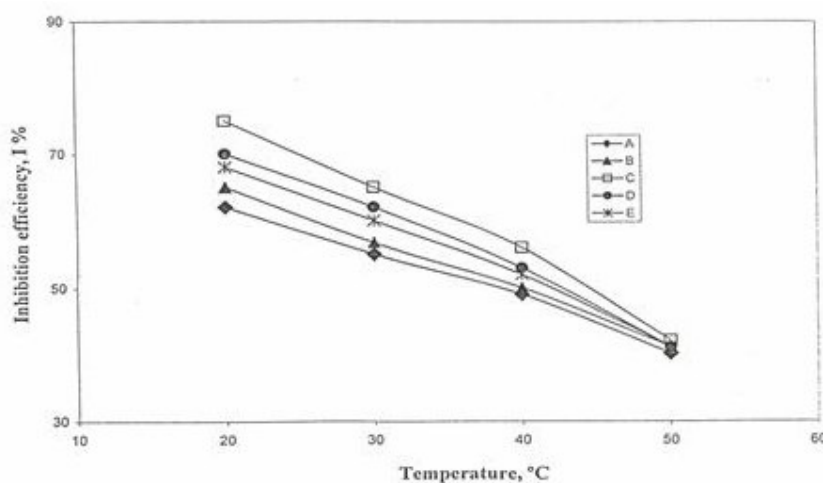


Figure 1. Relation between inhibition efficiency and temperature for muntz alloy in 1.0 M HCl in presence of 2×10^{-6} M of each extract.

Fig. 2 shows the effect of the concentration of extracts on the inhibition efficiency ($I \%$) in 1.0 M HCl at temperature of 20 °C. These results show that the increase of concentration of the extract increases the inhibition efficiency for the investigated extracts till reaching a limiting value. The values of the inhibition efficiency, $I\%$, were found to depend on the type of the extract under investigation. The order of inhibition efficiency decreases according to the order: $C > D > E > B > A$.

The obtained results showed that the increase of temperature increases the rate of corrosion and decreases the inhibition efficiency of the investigated extracts. The corrosion reaction can be regarded as an Arrhenius type process, the rate of which is given by the equation:

$$R_w = A \exp(-E_a^* / RT) \quad (2)$$

where R_w is the rate of corrosion ($\text{mg}/\text{cm}^2 \cdot \text{h}$), A is the Arrhenius pre-exponential constant, E_a^* is the activation energy for the corrosion process, and T is the absolute temperature.

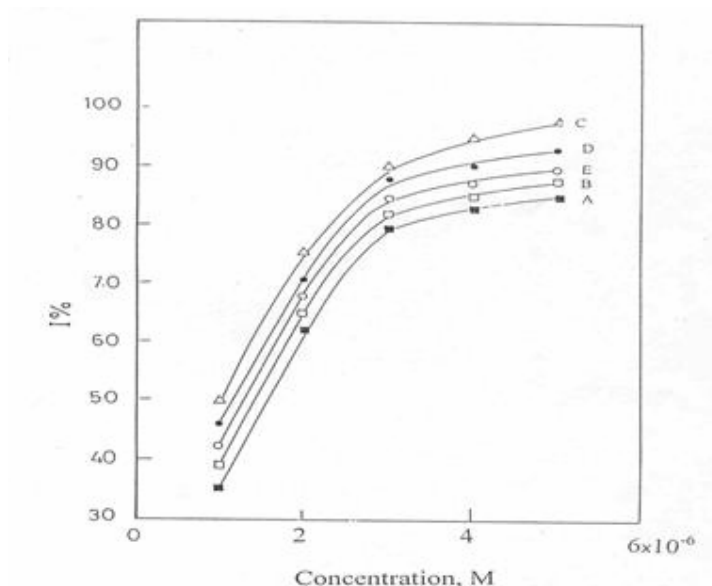


Figure 2. Effect of extracts concentration on inhibition efficiency at 20 °C (weight loss measurements).

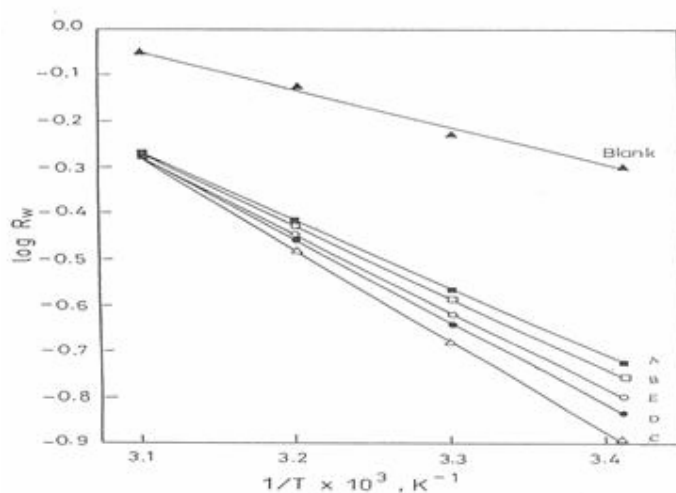


Figure 3. Arrhenius plot for muntz alloy in 1.0 M HCl in absence and presence of 2×10^{-6} M of the investigated extracts.

Fig. 3 represents the Arrhenius plots of the logarithm of corrosion rate (R_w) versus $1/T$ for the muntz alloy immersed in 1.0 M HCl in the absence and in the presence of 2×10^{-6} M of each of the investigated extracts. The values of E_a^* were calculated from the slopes of these plots and listed in Table 2. Note first that E_a^* values are low, indicating fast corrosion of muntz in 1.0 M HCl solutions. These values may be compared with a value of 70 kJ/mole for the corrosion of mild steel in 2 M HCl (uninhibited) [35] and a value of 76 kJ/mole for corrosion of steel in 1.0 M H_2SO_4 in the presence of 10^{-3} M imidazole [36]. In addition, the

E_a^* values increase in the same order as the inhibitory efficiency, i.e., the better inhibitors show the highest values of activation energy for the corrosion process [37,38]. This indicates that the energy barrier for the corrosion reaction increases in the presence of these extracts. It means that by addition of the inhibitor in the acid solution, the corrosion reaction will be further pushed to surface sites that are characterized by higher values of E_a^* , indicating that corrosion occurs at the uncovered part of the surface.

Table 2. Different values of E_a^* for muntz alloy in 1.0 M HCl in the absence and in the presence of 2×10^{-6} M of extracts.

Inhibitor	E_a^* / (kJ/mol)
Blank	15.10
A	27.04
B	28.93
C	36.99
D	32.80
E	31.30

b - Polarization measurements

Fig. 4 represents the galvanostatic anodic and cathodic polarization curves for the muntz alloy immersed in 1.0 M HCl in the absence and in the presence of different concentrations of extract A at the temperature of 20 °C. Similar polarization curves are obtained in the presence of other extracts, but not shown. From these polarization curves the different values of corrosion current density, i_{corr} , and corrosion potential, E_{corr} , were deduced by extrapolating Tafel's lines and listed in Table 3 for the investigated extracts (A- E). The different values of inhibition efficiency, I %, were calculated from the corresponding corrosion current densities, i_{corr} , using the following equation:

$$I \% = \left[1 - \frac{(i_{corr})_{inhi}}{(i_{corr})_{free}} \right] * 100 \quad (3)$$

where $(i_{corr})_{free}$ and $(i_{corr})_{inhi}$ are the corrosion current densities in the absence and in the presence of the inhibitor, respectively. The calculated values of I % are listed in Table 3 for the different concentrations.

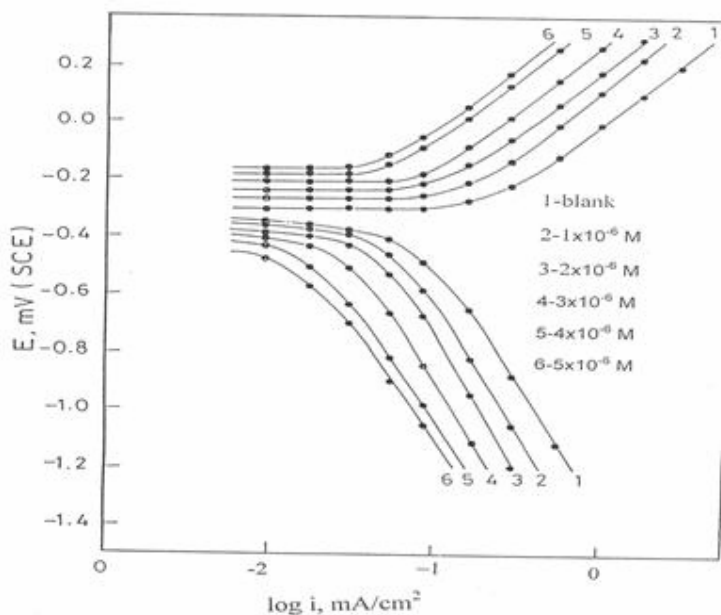


Figure 4. Galvanostatic cathodic and anodic polarization curves for muntz alloy in 1.0 M HCl in absence and presence of different concentrations of extract A at 20 °C.

Table 3. Galvanostatic polarization data for muntz alloy in 1.0 M HCl solution in the absence and in the presence of different concentrations of extracts (A-E) at 20 °C.

Concentration (M)	E_{corr} (mV)	A		B		C		D		E	
		i_{corr}	I%	i_{corr}	I%	i_{corr}	I%	i_{corr}	I%	i_{corr}	I%
0.00	-300	70.0	—	70.0	—	70.0	—	70.0	—	70.0	—
1×10^{-6}	-290	46.2	34	42.0	40	34.3	51	37.8	46	39.9	43
2×10^{-6}	-280	27.3	61	24.5	65	16.8	76	20.3	71	21.7	96
3×10^{-6}	-270	14.0	80	11.9	83	06.3	91	08.4	88	09.8	86
4×10^{-6}	-260	11.9	83	09.8	86	02.8	96	06.3	91	08.4	88
5×10^{-6}	-250	10.5	85	07.0	90	00.7	99	04.2	94	06.3	91

Fig. 5 represents the effect of the addition of increasing amounts of the investigated extracts on the values of inhibition efficiency (I %) for the muntz alloy at the temperature of 20 °C. The plots of Fig. 5 indicate that the value of I% increases with the increase of the amount of the additive reaching limiting values. Also, these results indicate that at a given concentration the value of inhibition efficiency, I %, for the investigated extracts decreases according to the order: C > D > E > B > A. This order is coincident with that obtained by weight loss measurements.

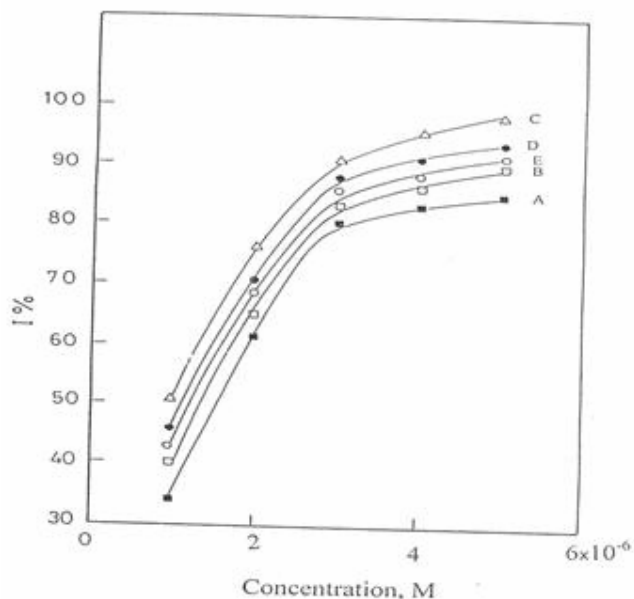


Figure 5. Effect of extracts concentration on the inhibition efficiency at 20 °C (polarization measurements).

The plots of Fig. 4 and similar ones indicate that the investigated extracts behave as mixed inhibitors, i.e., both the cathodic and anodic polarization curves are affected by the presence of these extracts in the corrosion solution. Also, it has been found that the magnitude of the displacement of the polarization curves appears to be dependent on the type and concentration of the extract. The cathodic and anodic polarization curves gave rise to more or less parallel Tafel's lines, indicating that the hydrogen evolution and metal dissolution were activation controlled and the addition of the investigated extracts did not modify the mechanism of these processes.

c - Linear polarization measurements

Fig. 6 represents potential-current plots for the muntz alloy immersed in 1.0 M HCl solution in the absence and in the presence of increasing amounts of the extract A. Similar plots are obtained for the other extracts, but not shown. From the plots of Fig. 6 and similar ones the values of linear polarization ($R_p = \Delta E / \Delta i$) were calculated and listed in Table 4. The values of inhibition efficiency, I%, were calculated from linear polarization, R_p , using the following equation:

$$I \% = \left[1 - \frac{(R_p)_{free}}{(R_p)_{inhib}} \right] * 100 \quad (4)$$

where $(R_p)_{free}$ and $(R_p)_{inhi}$ are the linear polarization in the absence and in the presence of inhibitors, respectively. The calculated values of I% for the investigated extracts (A– E) are listed in Table 4.

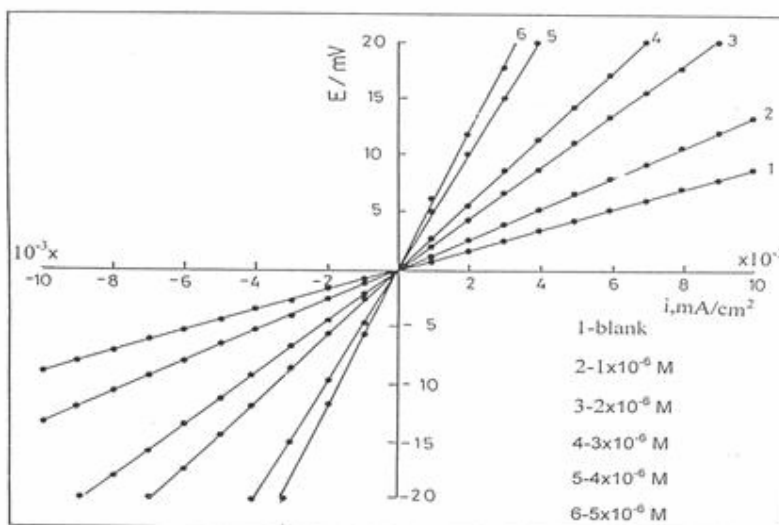


Figure 6. Potential-current plots for the muntz alloy in 1.0 M HCl solutions in absence and presence of different concentrations of extract A at 20 °C.

Table 4. Data of linear polarization measurements for muntz alloy in 1.0 M HCl solution in the absence and in the presence of different extracts (A-E).

Concentration (M)	A		B		C		D		E	
	R_p (Ω/cm^2)	I%	R_p (Ω/cm^2)	I%	R_p (Ω/cm^2)	I%	R_p (Ω/cm^2)	I%	R_p (Ω/cm^2)	I%
0.00	900.0	–	900.0	–	900.0	–	900.0	–	900.0	–
1×10^{-6}	1343.3	33	1475.4	39	1800	50	1636.36	45	1551.7	42
2×10^{-6}	2250.0	60	2500.0	64	3600	75	3000.0	70	2812.5	68
3×10^{-6}	2903.2	79	5294.2	83	9000	90	7500.0	88	6000.0	85
4×10^{-6}	5000.0	82	6428.57	86	18000	95	10000	91	7500.0	88
5×10^{-6}	6000.0	83	10000	91	45000	98	15000	94	11250	92

Fig. 7 represents the effect of the addition of increasing amounts of the investigated extracts (A –E) on the values of I% for the muntz alloy at the temperature of 20 °C. The plots of Fig. 7 indicate that I% for the extracts increases with increasing the amount of the additive reaching limiting value. Also, the inhibition efficiency decreases according to the order: C > D > E > B > A. This order is coincident with those obtained by weight loss and galvanostatic polarization measurements.

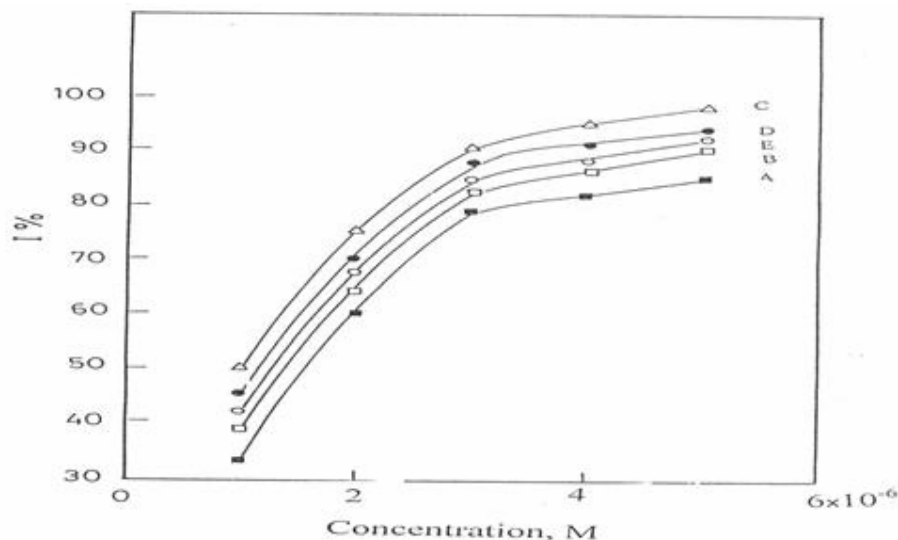
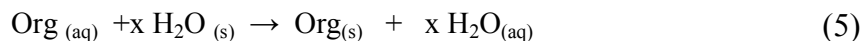


Figure 7. Effect of extracts concentration on the inhibition efficiency at 20 °C (linear polarization measurements).

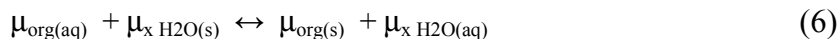
The difference in inhibition efficiencies of the investigated water extracts may be accounted by the fact that, as above mentioned, each extract contains a large number of compounds, which are present in different amounts depending on the type of extract. From the experimental results it was found that the net effect of these compounds was a retardation of the dissolution process of the alloy in HCl solution. It can be proposed that the effective compounds in these extract contain functional groups, which can operate as adsorption centers.

From the above-mentioned discussion, it is clear that the compounds present in the investigated extracts contain sulphur or oxygen and may contain nitrogen atoms, which can be used as adsorption centers. The shape of the molecule and its size, and the presence of conjugate double bonds and other groups (such as CH_3O^- , OH), determine the electron density on the adsorption centers and consequently the strength of the extract on the metallic surface. This reflects the observed differences in the efficiency of inhibition between the various extracts and leads to the order: $C > D > E > B > A$. This order indicates that the water extract of the cloves of garlic bulb (C) has the highest inhibition efficiency on the corrosion of the muntz alloy in HCl. This effect may be attributed, as above mentioned, to the presence of more than one sulphur compound in the extract and also to the presence of conjugate double bonds in these compounds. Also, the increased inhibition efficiency of water extract of orange peels (D) on the corrosion of alloy in HCl may be attributed to the presence of methoxy groups ($-\text{OCH}_3$) in the active compound. The presence of these methoxy groups in the inhibitor greatly increases the electron density on the adsorption centers and renders the active compound to behave as a hard base.

The adsorption of an organic adsorbate on the surface of a metal can be regarded a substitutional adsorption process between organic compound in aqueous phase and water molecules adsorbed on the electrode surface [39]



where (x) is the size ratio, which is the number of water molecules replaced by one molecule of organic adsorbate. The above process attains equilibrium when:



where μ is the chemical potential.

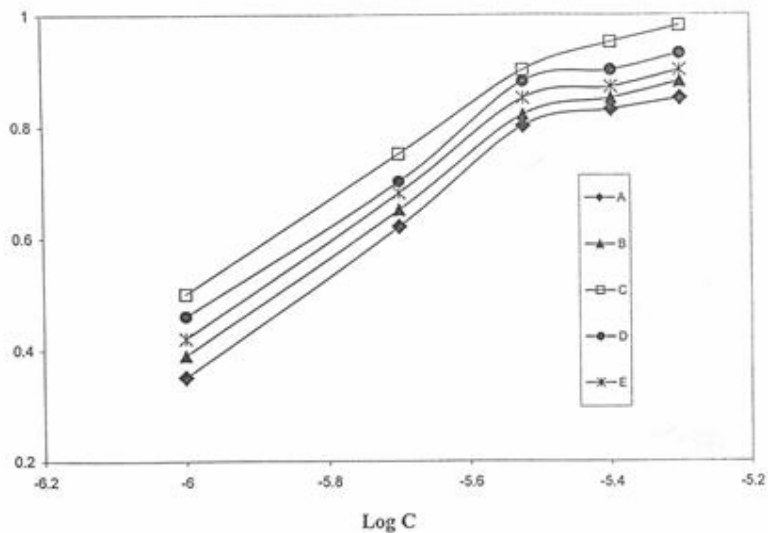


Figure 8. Frumkin's adsorption isotherm for extracts on muntz alloy from 1.0 M HCl solution at 20 °C.

The plots of θ (where $\theta = I/I_0$) versus $\log C$ are depicted in Fig. 8 at the temperature of 20 °C. The values of θ and C were taken from weight loss measurements. Similar plots can be obtained for the values of θ , obtained from the galvanic polarization and linear polarization measurements. From these plots, it is found that the Frumkin's isotherm is the most suitable for the adsorption process of the investigated extracts onto the muntz alloy. The relation between θ and $\log C$ gives S-shape curve. The Frumkin's isotherm can be expressed by the following equation:

$$\ln KC = a \theta \quad (7)$$

where θ is the surface coverage, K is the equilibrium constant of the adsorption process, a is the molecular interaction parameter, and C is the inhibitor concentration.

In Cu-Zn alloy system, Zn forms an ordered solid solution up to 39 wt% Zn. Electrochemically Zn has a more active electrode potential than Cu. Hence brasses have been found to suffer dealloying due to the preferential removal of Zn from the surface of the alloy. The rate of dealloying has been found to increase with the increase of Zn content of the alloy. It is evident that the chemical composition of the alloy and its metallurgical structure play a vital role in controlling the dezincification in brasses. Literature survey on dealloying of brasses shows that a number of hypotheses have been proposed to explain the

mechanism of the loss of Zn under specified experimental conditions; these mechanisms are:

- (i) preferential dissolution of Zn from the surface of the alloy;
- (ii) simultaneous dissolution of both Cu and Zn followed by the redeposition of copper;
- (iii) a combination of both the above mentioned processes.

Table 5. Results of atomic absorption analysis of the aggressive solution (1.0 M HCl) in the absence and in the presence of 2×10^{-6} M of each extract, after two hours exposure time.

Aggressive solution	Weight loss/ (mg)	Amount of Zn ²⁺ / (mg)	Amount of Cu ²⁺ / (mg)
Blank	10	10 (100%)	-
Blank +A	3.8	2.32 (61%)	1.485 (39%)
Blank +B	3.5	2.064 (59%)	1.437 (41%)
Blank +C	2.5	1.319 (52.75%)	1.1825 (47.25%)
Blank +D	3	1.67 (55.67%)	1.33 (44.33%)
Blank +E	3.2	1.83 (57.18%)	1.37 (42.82%)

In acidic solutions zinc dissolves preferentially first from the surface of the alloy. The rate of dezincification decreases with time and at a later stage simultaneous dissolution of both copper and zinc takes place. Table 5 shows the results of the atomic absorption spectroscopic measurements carried out on the aggressive solution (1.0 M HCl) in the absence and in the presence of 2×10^{-6} M of each of the investigated extracts for the determination of zinc and copper after two hours exposure time. These results indicate that in 1.0 M HCl solutions, without extracts, zinc preferentially dissolves from the alloy (as indicated from the presence of zinc only in the solution after the exposure time). The presence of the investigated extracts in the aggressive solution greatly inhibits the process of preferential dissolution of zinc from the alloy and the simultaneous dissolution of both zinc and copper takes place instead. The extent of preferential dissolution of zinc of the alloy greatly depends on the type of the extract and decreases according to the order: A > B > E > D > C. This order is the same as that of the inhibition efficiency of these extracts. This means that these extracts inhibit the general corrosion of the alloy, but also inhibit the process of dezincification of the muntz alloy.

Conclusions

- 1- There is a good agreement among the results obtained by different techniques of measurements.
- 2- The investigated water extracts have high inhibitory effect on the corrosion of muntz alloy in 1.0 M HCl.
- 3- The inhibitory efficiency greatly depends on the type and concentration of the extracts, decreasing according to the order: C > D > E > B > A.
- 4- The inhibitory effect of the investigated extracts results from their adsorption on the metallic surface according to the Frumkin's isotherm.
- 5- The presence of extracts in the corrosive medium decreases the values of activation energy of corrosion.
- 6- The investigated inhibitors greatly inhibit the process of preferential dissolution of zinc from the alloy in the aggressive solution.

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