

IRAQI ORANGE PEEL EXTRACT INHIBITS CORROSION OF METALLIC ALLOYS IN HYDROCHLORIC ACID SOLUTION

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Abstract

The main purpose of this work is to investigate the properties of Iraqi orange peel extract as an inhibitor of corrosion of metallic alloys (low carbon steel (**SAE AISI 1018 steel**), copper alloy (α -Brass) C27400 and aluminium alloy (EN AW-5083)) in 0.5 M hydrochloric acid medium. The mass loss test and electrochemical test were used to assess the extent of corrosion in the presence of orange peel extract, and various kinetic and thermodynamic parameters were calculated and discussed in order to understand the corrosion and inhibition mechanism. For all metallic alloys studied, the corrosion rate decreased as the concentration of orange peel extract increased. It was also found that the corrosion rate decreased in line with the length of exposure of the alloy to the orange peel extract. As a result of using the Iraqi orange peel extract with a concentration of 500 ppm in the 0.5 M HCl acid, it led to a reduction in the corrosion rate of low carbon steel from 12.37 to 5.34 mpy, while in case of α -Brass Alloy the corrosion rate decreased from 1.44 to 0.34 mpy, either in the case of using 5038 aluminium alloy, the corrosion rate decrease from 71.123 to 19.678 mpy. These results suggest that the adsorption of orange peel extract on the surface of the metallic alloys leads to the formation of a protective layer that inhibits the action of the hydrochloric acid solution, and this layer develops in thickness and effectiveness as the immersion time increases.

Keywords: Al-alloy 5083, Brass alloy, Low carbon steel, Natural Inhibitor, Orange peel extract.

1. Introduction

Corrosion is the deterioration of the properties of a material because of chemical or electrochemical interaction with its medium [1]. The type of material and the environmental situation affect the nature and rate of this deterioration. Corrosion causes significant financial, human and, environmental losses, and as a result, it is associated, directly and indirectly with large economic costs. There are a number of ways of preventing corrosion depending on the environment in which the material is placed. These include anodic protection, cathodic protection, coatings, and the addition of Inhibitors. An inhibitor is a substance which, when added to a material at risk of corrosion, effectively decreases the dissolution thereby reducing the rate of corrosion [2-10].

Carbon steels, aluminum alloys, and copper alloys are very important alloys for industrial applications. In this role, they can be exposed to a variety of corrosive environments such as acid solutions. Indeed, acid solutions such as HCl, are widely used in many industrial systems [9]. For these reasons, many attempts have been made to find ways to reduce the costs arising from corrosion of such alloys. One of the most important tools to achieve this protection is the use of inhibitors. The choice of the most appropriate inhibitor, however, depends on the match between the chemical action of the inhibitor and the specific corrosive environment in which the alloy is placed.

The literature contains many studies exploring the inhibition of corrosion in acidic media, especially in respect of metals in industrial applications, in order to determine the rate of corrosion. Generally, these show that organic inhibitors are deleterious to the medium as well as being toxic. Natural inhibitors, however, are usually economic, nontoxic and eco-friendly, and therefore tend to be preferred [11]. Several studies have investigated the use of so-called “green” inhibitors that have been extracted from the seeds and leaves of plants [10-17], and, in recent years, several inhibitors have been synthesized from active compounds from plants [18-27].

One interesting example of such an inhibitor, is the peel of the citrus fruit, *Citrus sinensis*, popularly known as sweet orange [28]. Orange peel extract has been shown to be a good inhibitor of corrosion in mild steel [29-30].

The current study, therefore, aimed to investigate the inhibitive behaviour of orange peel on the corrosion of low carbon steel, brass alloy and 5083 Al-alloy in a solution of hydrochloric acid, as well as this research is an attempt to use orange peel waste as a corrosion inhibitor for metallic alloys within the directions of sustainable engineering and environmental protection.

2. Experimental Work

2.1. Chemical composition analysis of the metallic alloys

Samples of a low carbon steel, copper- alloy (α -Brass) C27400 and aluminium alloy (EN AW-5083) were used in this experiment. Each sample was 1mm thick and 10 mm in diameter. The chemical composition analysis of each material is shown in Tables 1 to 3. This analysis was performed using atomic absorption spectroscopy (Shimadzu AA7000).

Table 1. The chemical composition of low carbon steel, Wt. %.

Element	C	Mn	Ni	Cu	Si	S	P	Fe
Current Alloy	0.17	0.75	0.13	0.09	0.05	0.03	0.01	Rem.
Standard Alloy (SAE AISI 1018 steel)	0.15-0.20	0.60-0.90	-	-	≤ 0.05	≤ 0.05	≤ 0.04	Rem

Table 2. The chemical composition of α -brass alloy, Wt. %.

Element	Cu	Al	Fe	Pb	Ni	Sn	Zn
Current Alloy	63.00	0.05	0.05	0.08	0.03	0.06	Rem.
Standard Alloy (α-Brass) C27400	61.00-64.00	-	≤ 0.05	≤ 0.09	-	-	Rem.

Table 3. The chemical composition of alloy 5083, Wt. %

Element	Mg	Mn	Fe	Zn	Cr	Si	Ti	Cu	Al
Current Alloy	4.2	0.70	0.35	0.30	0.15	0.12	0.07	0.06	Rem.
Standard EN AW-5083	4.0-4.9	0.4-1.0	0.40	0.25	0.05-0.25	0.40	0.15	0.10	Rem.

2.2. Specimen preparation

Cylindrical specimens of the metallic alloys, each with a 1mm thick and 10 mm in diameter, were used in the mass loss measurement and electrochemical test. Before the test, the specimens were polished with Emery papers (220, 400, 600, 800 and 1000 μm), degreased with boiling benzene, washed with distilled water, then dried and put in vacuum desiccators.

2.3. Preparation of orange peel extract

The orange (*Citrus sinensis*) fruits (used in this study) were obtained from local markets within Diyala Province, in central Iraq. The orange was first flushed by supply water and then washed in distilled water three times before peeling, the peel fractions were carefully separated, dried at 50 °C using an electric oven and then ground using a home grinder. A 5 gram was weighed and mixed with 50 ml of the selected solvents (distilled water, hydroethanolic solution (1:1 v/v) and diluted hydrochloric acid (5% with distilled water)). The solution was then divided into small enough portions for Soxhlet extraction. Ethanol was selected as the solvent in the Soxhelt extractor and the peel samples were left in the extractor for six hours. After this, a blend of solvent and orange peel extract was retrieved. This was placed in a rotary evaporator (Stuart-400RE) in order to obtain a solid orange peel extract. The solid extract powder was saved in a desiccator until the tests were conducted.

2.4. Detection of active compounds of the orange peel powder

Fourier Transform Infrared (FTIR) was used to detect the active compounds in the orange peel extract powder. Orange peel extract was characterized by used type (IRA ffinity-1, Shimadzu) with a diamond crystal. A diamond crystal was used for the collection of the background spectrum.

The sample of orange-peel powder was mixed with potassium bromide (*KBr*), in a 1:20 ratio and then pressed to a tablet form. The spectra were recorded with a range of 500 to 4000 cm^{-1} .

2.5. Corrosion testing

2.5.1. Mass loss test

The mass loss test was carried out by immersing the metallic alloy samples in 0.5 M HCl acid solution at a temperature of $(25 \pm 2)^\circ\text{C}$. This solution variously contained no inhibitor (the control solution) and then different concentrations of orange peel extract (100, 300 and 500 ppm) for periods ranging from 24 hours to 360 hours, with the mass being registered before and after each 24 hour periods. The mass loss measurements were acquired in accordance with ASTM G31-72 [31], using a sensitive balance with an accuracy of ± 0.1 mg. The corrosion penetration rate (*CPR*) was calculated from the mass loss test in mils per year (mpy) using the relationship [1]:

$$CPR = \frac{534 M}{\rho A t} \quad (1)$$

where *M* : Mass loss by corrosion (mg), ρ : Density of metallic alloy (mg/cm^3), *A* : Exposed surface area (in^2), and *t* : Immersion time (h).

2.5.2. Electrochemical corrosion test

Potentiodynamic polarization tests were also conducted in order to determine the corrosion parameters and the behaviour of the metallic alloy when exposed to the HCl solution and orange peel extract. 10 mm×10 mm×3 mm samples were cut from the alloys using a wire-cut electron discharge machine (EDM). These specimens were then polished with Emery papers of various grit size (150, 320, 600, 800, 1000, 1200 and 1500 μm) and cleaned both ultrasonically and in a bath of distilled water.

The potentiodynamic polarization cell consists of a working electrode, a reference electrode (saturated calomel electrode) and a counter electrode (platinum) in a fully aerated condition. A test temperature of $(25 \pm 2)^\circ\text{C}$ was preserved for the experimental work utilizing Cyber Lab CB 2000. An open circuit potential (*OCP*) calculation was carried out so as to stabilize the potential for 2 hours in all cases. Both the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}), were measured using the Tafel method. The polarization resistance (*R_p*) was determined from Eq. (2) [1].

$$R_p = \frac{\beta_a \beta_c}{2.303 I_{corr} (\beta_a + \beta_c)} \quad (2)$$

where β_a is the anodic polarization slop, β_c is the cathodic polarization slop, and I_{corr} is the corrosion current density.

The inhibition efficiency (*E*%) was determined from the corrosion rate values before and after inhibition according to Eq. (3) [1].

$$E \% = 1 - \frac{CR_2}{CR_1} \times 100 \quad (3)$$

where CR_1 and CR_2 are the corrosion rate of the uninhibited and inhibited specimens.

The tests were carried out at a scan rate of 0.4 mV/s. The corrosion rate from the electrochemical test was calculated in accordance with ASTM G102- 89 [32].

3. Results and Discussion

3.1. Characterization of the orange peel powder - FTIR

The orange peel extract presented as a yellow powder with the FTIR spectrum was shown in Fig. 1. This spectrum shows a powerful absorption at 3414 cm^{-1} which is caused by a functional group of OH [33]. The broad peak at 2926 cm^{-1} shows the absorption of an aromatic C-H band in stretching mode. The wave numbers 1747 and 1635.64 cm^{-1} can be assigned to the extending peaks from the carbonyl group and C=C, respectively. The absorption peak at 1440.83 cm^{-1} , meanwhile, shows C=C stretching vibration. The peaks occurring at 1373.32 and 1234.44 cm^{-1} signal the existence of C-SO₂-Cl and aryl OH. Finally, the absorption at 1099.43 and 1055.06 cm^{-1} , displays the stretch peak of C-O [33]. This characterization therefore shows that the active groups in the orange peel powder are predominantly aldehydes, amines, ketones, alcohols and polyamides, or admixtures of phenolics and aromatics. These chemical compounds have inhibitory characteristics and the results overall are in line with those recorded by other investigators [33, 34]. The existence of double and triple bonds, and aromatic rings serve to modify the blocking action of orange peel powder extract [34-36].

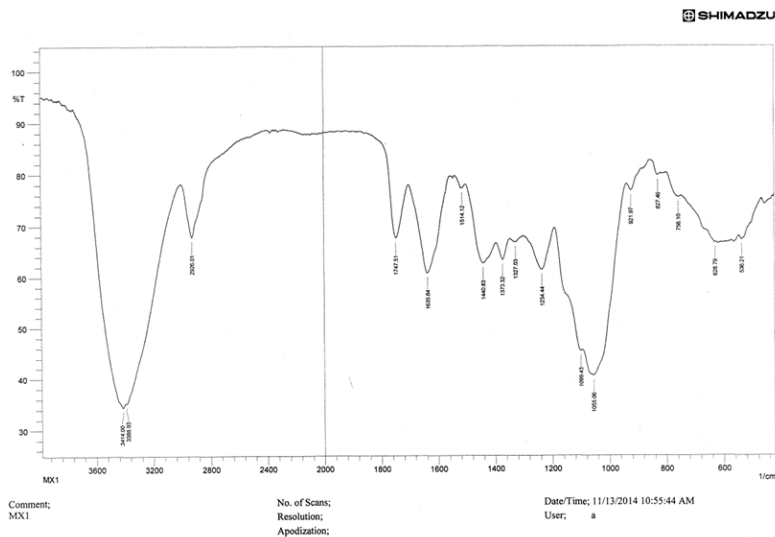


Fig. 1. FTIR spectra of orange-peel extract.

3.2. The mass loss test - Effect of orange peel extract on the corrosion resistance of metallic alloys

The following results were obtained when the metallic alloys specimens were immersed of the metallic alloys specimens in a hydrochloric acid solution containing different concentrations of inhibitors (100, 300 and 500 ppm of orange peel) for various periods from 24 hours to 360 hours.

a) Carbon Steel

Hydrochloric acid accelerates the corrosion of carbon steel due to the fact that the hydrogen ion (H^+) has an electrode voltage (E_o) of 0 V compared to - 0.44 V for iron ion (Fe^{2+}). On continuous exposure, the hydrogen ion behaves as an oxidizing agent accelerating the corrosion process by stimulating the dissolution of carbon steel. The chloride ion also accelerates the process of corrosion by combining with iron ion (Fe^{2+}), to create, ferrous chloride ($FeCl_2$) as shown by Eq. (4) [37].



This further stimulates the dissolution of carbon steel by dissolving back in to the solution and leaving the carbon steel surface open for more attacks from the oxidizing agent. Adding an inhibitor added to the acid solution will decrease the ability of the acid to attack the surface of the carbon steel. This reaction rate depends on several variables including the chemical composition of carbon steel, the type of adherent of oxides on the surface of the carbon steel, the immersion time, the solution temperature, acid concentration, the rate of stirring of the solution, the concentration of ferrous chloride, as well as inhibitor type and concentration.

Figure 2 shows the relationship between the *CPR* and immersion time in HCl-acid, both - without the natural inhibitor and with different concentrations of the inhibitor in 0.5 M HCl at 25 °C after (24, 180, and 360 h). Figure 2 shows that when the sample is immersed in HCl acid solution, there was a high rate of corrosion at the beginning of immersion as a result to a decrease in mass; this is due to increasing low carbon steel dissolution because increasing both acidity and Cl^- ion concentration [38]. With increasing immersion time, the *CPR* begins to decrease due to the effect of the deposition of corrosion products on the surface, while when the specimens were submerged in a hydraulic acid solution, containing concentrations of 100 or 300 ppm of orange peel extract, there was a significant reduction in the *CPR* compared to specimens submerged without inhibitor, as shown in Fig. 2. Furthermore, the reduction in the *CPR* was even greater when the concentration of orange peel extract was increased to 500 ppm.

These results suggest that the orange peel extract is adsorbed onto the surface of the low carbon steel surface, forming a suitable protective layer that blocks the oxidising activity of the HCl.

Furthermore, the reduction in the *CPR* was even greater when the concentration of orange peel extract was increased to 500 ppm. These results suggest that the orange peel extract is adsorbed onto the surface of the low carbon steel surface, forming a suitable protective layer that blocks the oxidising activity of the HCl.

The results of the current research were compared with references [28, 29] with regard to the use of orange peel extract as a corrosion inhibitor for carbon steels although the present research concerns for low carbon steel, the results were almost identical.

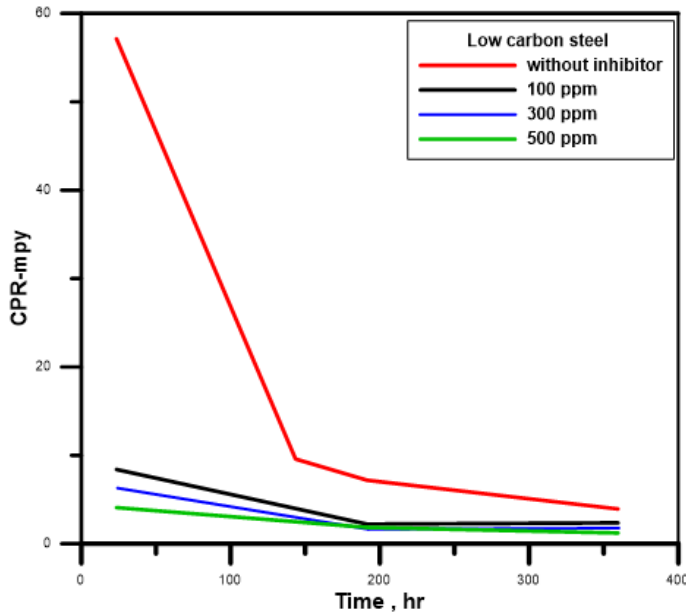
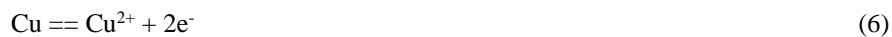


Fig. 2. The relationships between corrosion penetration rate and immersion time for low carbon steel.

b) α -Brass Alloy

Figure 3 shows the variation in at the CPR versus time for α -brass alloy in 0.5 M HCl solution without orange peel extract, and with 100 ppm, 300 ppm and, 500 ppm of orange peel extract. α -Brass alloy consists of about 70% copper and 30% zinc in a solution of hydrochloric acid, therefore, where the most active element in respect to corrosion is zinc, which is released into the solution faster than copper. The chemical reactions can be expressed by the following chemical equations [39, 40]:



The chemical reactions above lead to the formation of a blue solution in the hydrochloric acid solution due to the presence of divalent copper ions [40]. Yellow chloride precipitates were also observed on the surface of the brass as corrosion products. The *CPR* of brass increases in a linear manner with time, because of the persistent dissolution of copper ions and zinc ions participation in the anodic dissolution of the brass alloy.

On the other hand, the presence of 100 ppm orange peel extract significantly reduces the mass loss of brass alloy, and this was further reduced as the concentration of orange peel extract was increased to 300 ppm and then 500 ppm, as shown in Fig. 3. This is due to the adsorption of the orange peel molecules on

the surface of the alloy, which reduces the dissolution of brass alloy by hindering the points at which corrosion take place, moreover, adsorption of orange peel extract on active anode sites in brass alloy enhances the inhibitor effect in reducing anodic corrosion process, where the peel works predominately as an anodic inhibitor, thereby explain why the rate of mass loss reduces with increased orange peel extract [20, 41- 44].

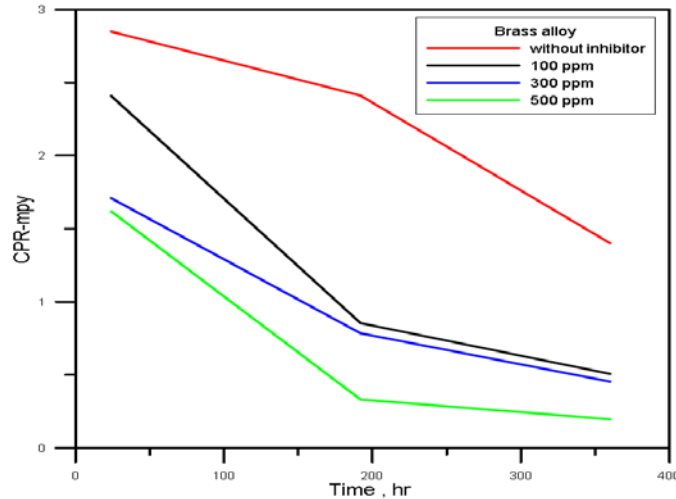


Fig. 3. The relationships between corrosion penetration rate and immersion time for α -Brass alloy.

c) 5083 Al-Alloy

The corrosion process of 5083 alloy involves the electrochemical process resulting from hydrochloric acid solution. This procedure can be expressed through the following [45]:

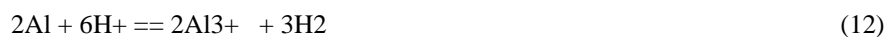
Oxidation



Reduction



The overall reactions can be written as follows:



The corrosion behaviour and inhibition activity of 5083 Al-Alloy submerged in 0.5 M HCl at 25 °C after (24, 180, and 360 h) is shown in Fig. 4. Figure 4 also shows a large loss of mass for the 5083 Al-alloy samples. This may be due to a local breakdown of the oxide layer because chloride ions have the potential to penetrate and damage this layer on the surface of alloy, thereby increasing the anodic solubility for Al and adsorption of depolarizing ions such as Cl⁻ [46].

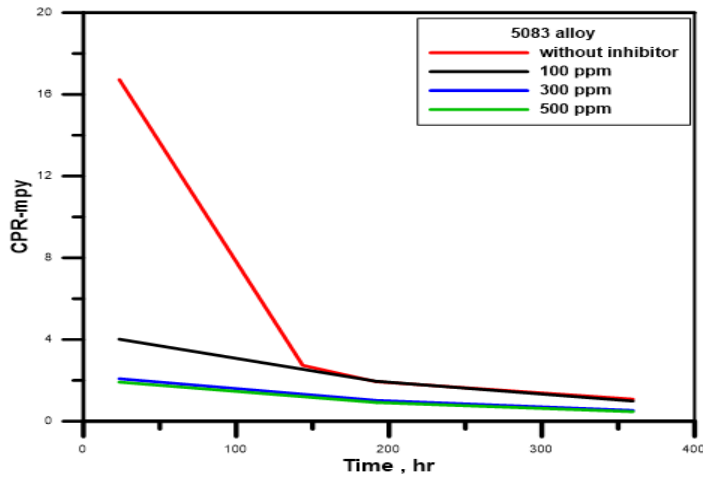


Fig. 4. The relationships between corrosion penetration rate and immersion time for Al-alloy 5083.

This is a result of adsorption on the inhibitor molecules on the alloy surface, creating aspiration of the alloy surface from the acid environment, thus protecting the alloy from corrosion. The energy barrier in this process rises in line with the concentration of inhibitor. The effect of inhibition on the corrosion resistance of the 5083 Al-alloy can be attributed to the adsorption of orange peel molecules on the alloy, limiting the disintegrating of the alloy by preventing decay locations and thereby reducing the mass loss.

3.3. The Electrochemical test results

Effect of orange peel extract on the corrosion behaviour of metallic alloys

a) Low carbon steel

The electrochemical action of the experimental low carbon steel with and without the presence of orange peel extract was investigated by Tafel potential polarization in 0.5 M HCl at 25 °C. The main parameters that can be obtained from these curves are the potential (E_{corr}) and current density (I_{corr}). As shown in Fig. 5 and Table 4, the corrosion current density decreases from 0.56 $\mu\text{m}/\text{cm}^2$ to 0.1 $\mu\text{m}/\text{cm}^2$ after inhibition, while the values for polarization resistance increased with the increase of orange peel extract concentration in HCl solution.

Figure 5 also shows that the corrosion current density of the inhibited specimen is lower while the potentials are higher when compared with the uninhibited specimen. This can be imputed to the rise in competitive adsorption of the extract of orange peel molecules on the alloy [47]. It was observed that the effect of orange peel extract on the anodic and cathodic behaviour over potentials is the same for both reactions, but the effect of the cathodic reaction is much less obvious (that is, the peel works predominately as an anodic inhibitor).

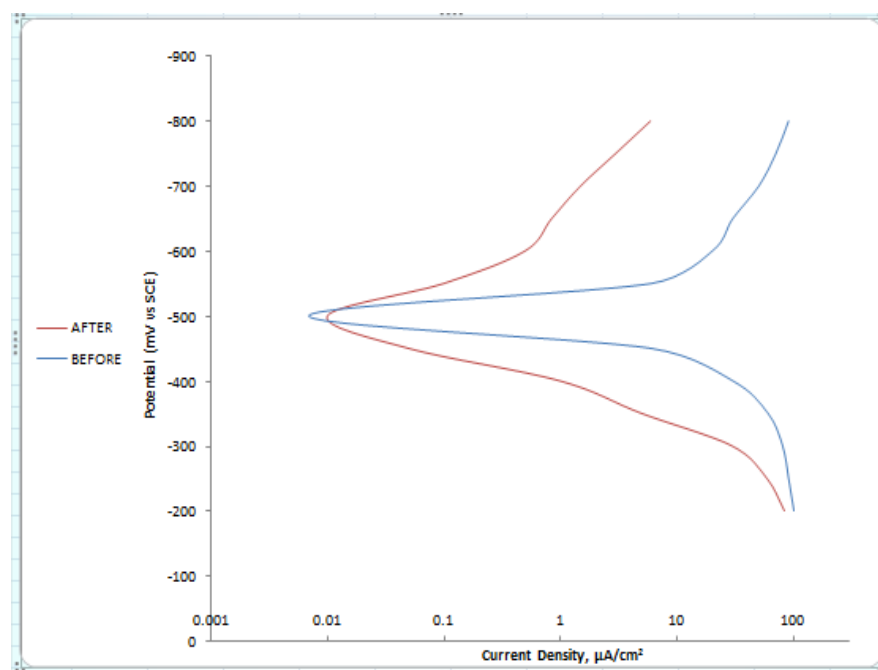


Fig. 5. Potentiodynamic polarization curves for low carbon steel in 0.5 M HCl solution before and after the addition of 500 ppm concentration of orange peel extract at 25° C and immersion time is 2 h.

Table 4. Kinetic electrochemical parameters results obtained from polarization curves for metallic alloys at absence and presence of 500 ppm of orange peel extract in 0.5 M HCl at 25°C.

Metallic Alloys	Inhibitor Conc. ppm	β_a mV/dec	β_c mV/dec	R_p $\Omega \cdot \text{cm}^2$	I_{corr} $\mu\text{A}/\text{cm}^2$	E_{corr} mV	CR mpy	Eff. %
Low Carbon Steel	0	95.0	323.0	1260.0	26.8	-688	12.37	----
	500	85.0	312.0	1910.0	11.6	-696.0	5.34	56.83
Brass Alloy	0	91.4	-135.0	284.40	3.25	-120.0	1.44	----
	500	72.3	-143.0	1744.0	0.74	-133.0	0.34	76.39
5083 Al Alloy	0	48.7	-149.3	10.821	3.72	-595.3	71.123	----
	500	28.6	-118.3	218.63	1.92	-655.4	19.678	72.33

b) α -Brass Alloy

Table 4 and Fig. 6 show the potentiodynamic polarization of α -Brass alloy in 0.5 M HCl with and without the presence of inhibitor. It can be seen that the cathodic polarization of the Tafel extrapolation plot does not change much with the increase in concentration of orange peel extract. The cathodic reaction in 0.5 M HCl is fundamentally due to oxygen reduction.

From Table 4, the values of polarization resistance increased with increased inhibitor concentration. Figure 6 and Table 4 also show that, the current density decreases from 0.05 $\mu\text{A}/\text{cm}^2$ to 0.005 $\mu\text{A}/\text{cm}^2$ as action of inhibition as well as can be inferred that E_{corr} is the function of in Cl^- . The increase in Cl^- shifts the E_{corr} in an active (negative) direction. The cathodic portion of the curve is almost an

activation-controlled process (just below the E_{corr}), while in the anodic portion the polarization is an activation- controlled process.

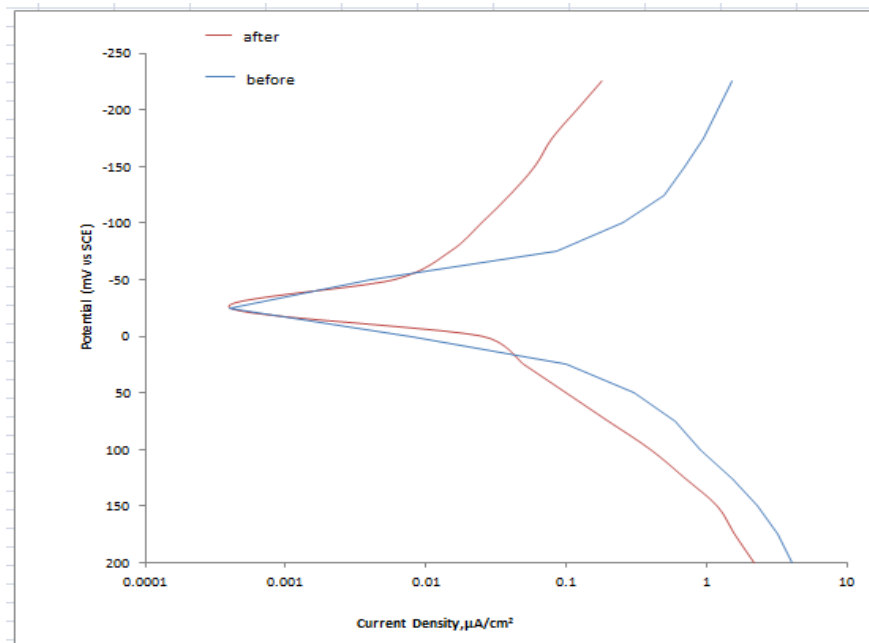


Fig. 6. Potentiodynamic polarization curves for α -Brass alloy in 0.5 M HCl solution before and after the addition of 500 ppm concentration of orange peel extract at 25° C and immersion time is 2 h.

The existence of the orange peel extract results in a marked decrease in current densities for both anodic and cathodic polarization, possibly as a result of adsorption of the organic admixtures found in the orange peel extract at the active locations of the copper electrode. The inhibition of both α -Brass alloy disintegration and oxygen reduction, thereby hinder the kinetics of corrosion [42].

c) 5083 Al-Alloy

Polarization plots for 5083 aluminium alloy in 0.5 M HCl with and without orange peel extract is shown in Fig. 7. It can be seen that the presence of the orange peel extract is associated with a decrease in the corrosion current density from $6.6 \mu\text{m}/\text{cm}^2$ to $5.8 \mu\text{m}/\text{cm}^2$, leading to a decrease in the corrosion rate. Figure 7 also shows that the cathodic part shifts to a more negative potential while the anodic part becomes more positive. Meanwhile, the corrosion current density becomes lower. Figure 7 and Table 5 also shows that the addition of the orange peel extract leads to lower currents in both the cathodic and anodic parts, perhaps due to the blocking influence of the adsorbed inhibitor molecules. The results in Table 4 indicate the improvement of polarization resistance when orange peel extract is added.

The cathodic reaction of the H_2 -gas molecule is produced through the capture of an electron liberated in the anodic process when 5083 Al-alloy is immersed in hydrochloric acid. The orange peel extract can affect the corrosion behaviour of

5083 Al-alloy by altering the electrochemical behaviour, which in turn influences the decay kinetics. The inhibitor molecules are adsorbed onto the positively-charged locations created on the surface of the alloy by the release of electrons from the alloy surface due to the action of HCl. The accretion of inhibitor molecules at this thin positive layer serves to separate the 5083 Al-alloy from the corrosive environment, preventing more ions from migrating from the alloy and reducing the corrosion rate [46].

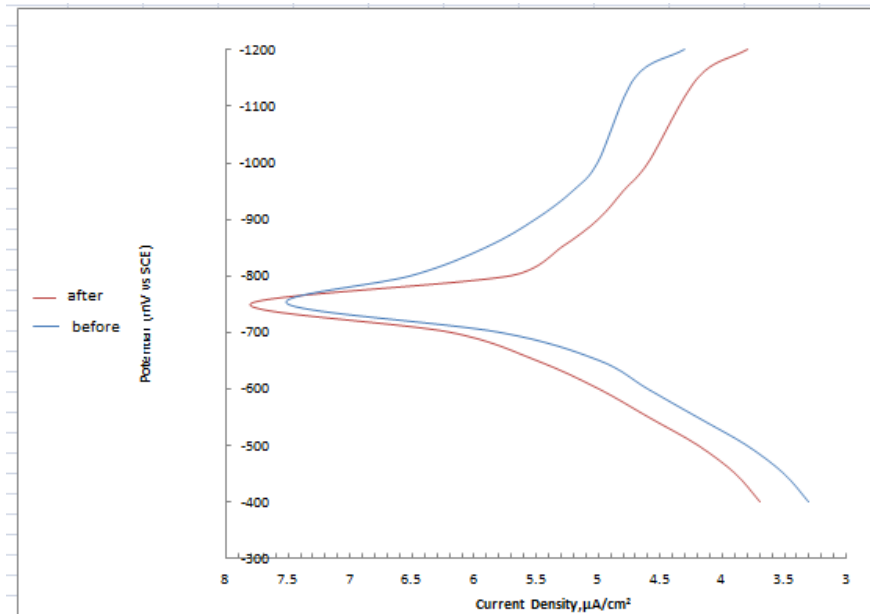


Fig. 7. Potentiodynamic polarization curves for 5083 Al- alloy in 0.5 M HCl solution before and after the addition of 500 ppm concentration of orange peel extract at 25° C and immersion time is 2 h.

4. Conclusions

The results obtained through this research study reveal that:

- The results of the mass loss test and electrochemical test are compatible with the possibility of using orange peel as a corrosion inhibitor for low carbon steel, brass alloy and 5083 Al-alloy in 0.5 M HCl.
- Reduction of mass loss of metallic alloys in hydrochloric acid increases as **the** concentration of the inhibitor increases.
- The inhibition activity increases with exposure time and causes the **creation** of a protective layer that develops with time. The efficiency of inhibition was the highest in the respect to brass alloy, up to 76.39 %, whereas the inhibition efficiency was about 56.83% for low carbon steel and, 72.33% for corrosion of the 5038 aluminium alloy.
- There is an excellent economic opportunity to use orange peel waste as an inhibitor material in the context of sustainable engineering and environmental protection.

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