# **Corrosion Inhibition of Carbon Steel in HCl Solution by Aqueous Brown Onion Peel Extract**

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The effect of aqueous brown onion peel extract on the corrosion process of carbon steel in 1 mol  $L^{-1}$  HCl was examined. The electrochemical results, including the displacement of the corrosion potential and the inhibitory action in both anodic and cathodic polarization curves showed that the examined extract acted as mixed-type inhibitor. The results of the electrochemical impedance measurements showed that the Rct values increased in the presence of inhibitor reaching 94% of inhibition efficiency in the presence of 300 mg  $L^{-1}$  of the extract. The inhibition efficiency of C-steel in 1 mol  $L^{-1}$  HCl increased as the temperature increased and the apparent activation energy (Ea) of C-steel dissolution decreased in the presence of the extract, which suggest a strong chemisorptive bond between the components present in the onion extract and the metal surface. The extract analysis showed few volatile compounds with 3(2H)-Furanone, 2-hexyl-5-methyl- as the major volatile compound and a nitrogenous base (5-octadecyl-pyrimidine-2,4,6-trione) which may play an important role in the inhibition process.

Keywords: Carbon Steel, Acid corrosion, Onion peel extract

# **1. INTRODUCTION**

Corrosion is a process that results from the action of the medium on a particular material, causing its overall, partial, superficial or structural deterioration by an electrochemical, chemical or electrolytic attack. Corrosion problems are common in oil industries, where approximately 50% of materials failures in oil refineries and petrochemical plants are caused by this phenomena, which promotes economic, environmental and human life losses [1].

Corrosion inhibitors are widely used in industries to combat metallic corrosion, as they are able to slow down and even eliminate the corrosive processes taking place in the transportation, production and storage of oil and its derivatives. The majority of inhibitors used in industry in acid corrosion are organic compounds consisted of nitrogen, oxygen and sulfur atoms. Inhibitors that contain double or

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triple bonds take an important part in facilitating the adsorption of these compounds onto metal surfaces as well, since a bond can be formed between the electron pair and/or the  $\pi$ -electron cloud of the donor atoms and the metal surface, thereby reducing corrosive attack in acidic media [2, 3].

The introduction of these compounds in the medium leads to an additional need for further treatment of the processing disposal systems, discharged as effluent. This treatment is necessary to ensure the maintenance of the permitted levels of elements or compounds, which are controlled by environmental legislation. The definition of appropriate technologies for the efficient treatment of wastewater is a decisive factor to the environmental licensing and commissioning of petrochemical plants.

Environmental sustainability concerns and the elevated costs of synthetic inhibitors motivated the search for less expensive and environmentally friendly alternatives such as corrosion inhibitors derived from natural products [3-30]. Besides, food-processing generates by-products and wastes which are rich in biocompounds that can offer a readily available natural source of antioxidants [23]. It is generally known that the yield of chemical extraction depends on the type of solvents with varying polarities, extraction time and temperature, sample-to-solvent ratio as well as on the chemical composition and physical characteristics of the samples [31]. In previous studies from our group [5-8], we observed that aqueous extracts of garlic peel, coffee grounds, fruit peels (mango, orange, passion fruit and cashew) and grape pomace, are very effective as corrosion inhibitors of carbon steel 1020 in aqueous 1 mol  $L^{-1}$  HCl. Additionally, corrosion inhibition efficiency might be higher than 97% depending on the concentration of natural extract added.

Almaraj *et al.* measured the efficiency of aqueous extract of *Allium cepa* (onion's inner part) as a corrosion inhibitor of carbon steel in ground water by weight loss method. The formulation consisted of 3 mL Allium cepa extract, 50 ppm of  $Zn^{2+}$  and 50 ppm of potassium sodium tartrate and resulted in 97% of inhibition efficiency. The authors showed synergistic effect between onion- $Zn^{2+}$ -tartrate system [27]. Red onion skin tannin has been found to be an effective corrosion inhibitor of aluminium in hydrochloric acid solution using gravimetric, thermometric, and UV/visible spectrophotometric techniques [28]. Aqueous onion peeled extract was also studied as a natural corrosion inhibitor in industrial chill wastewater system. Results showed that the optimum inhibition efficiency for iron, nickel and copper were 92%, 88% and 46%, respectively, when Allium cepa was present at 0.6 g/L [29]. Parikh *et al.* studied some natural compounds from onion (Allium cepa), garlic (Allium sativum) and bitte gourd (Momordica Charantia) as corrosion inhibitors of mild steel in HCl solution [30].

In this sense, the present work aims to investigate brown onion peel (*Allium cepa*), a common waste, as a natural inhibitor of carbon steel 1020 corrosion in HCl, and to study its composition, concerning the volatile compounds, which may present anti-corrosive activity.

## **2. EXPERIMENTAL**

# 2.1. Inhibitor preparation

Brown onion peel extracts were obtained by infusion in water. 200 mL of boiling distilled water were transferred over 5 g of ground onion peel and kept infusing for sixty minutes at room temperature. This extract was filtered and the liquid containing the biocompounds of interest for this

study was congealed. After frozen, the extract was taken over a lyophilization process in order to remove all the water content. The final powder obtained was used as a corrosion inhibitor for carbon steel in 1 mol  $L^{-1}$  HCl.

#### 2.2. HS-SPME GC-MS analysis of the brown onion peel extract

Volatiles from brown onion peel extract were analysed by head-space solid-phase microextraction gas-chromatography mass spectrometry (HS-SPME-GC-MS). One gram of the onion peel extract was transferred into 10 mL vial, sealed with aluminium seals with PTFE/silicone septa, and heated until equilibrium at 60 °C for 1 h, with constant stirring in a glycerine bath over a thermostated magnetic stirring plate. For headspace extraction, a divinylbenzene/carboxene/polydimethysiloxane fibre (DVB/CAR/PDMS, 50/30 µm, Supelco) was used. The DVB/CAR/PDMS fibre was preconditioned inside the GC-MS injection port for 30 min at 250 °C. The pre-conditioned fibre was exposed to the sample head-space for 15 min while the vial was kept at 60 °C. SPME extraction from the liquid onion peel extract was also tested, but results were not improved by this technique, and headspace extraction was adopted. The fibre was retracted and transferred immediately to the GC-MS injection port for desorption-injection, for 3 min at 260 °C.

The volatile compounds were analyzed in a Shimadzu GC-17A gas-chromatograph interfaced to a QP5050A Mass Spectrometer (MS) system and equipped with a capillary column (5% Phenyl-methylpolysiloxane, 30 m, 0.25 mm; Quadrex 007-5). The temperatures of the injector and the interface were both 260 °C. Helium was used as carrier gas. The column oven was temperature-programmed as follows: 30 °C for 10 min, temperature programmed at 3.0 °C/min to 245 °C and held for 10 min, for a total analysis time of 92 min. The mass spectrometer was operated at 70 *e*V as ionization energy, in scan mode from 40 to 500 amu, and at 1 scan/s. The identities of chromatographic peaks were determined based on software comparisons of unknown compounds mass spectra with those of the National Institute of Standards and Technology (NIST) mass spectral database. In addition, retention index (RI) of each compound was calculated using n-alkanes (C7–C30) as external references for comparisons with published data. Contents of volatile compounds were assessed by area normalization, and considered as semi-quantitative.

#### 2.3. Electrochemical procedure

The experimental procedure used in this study was the same used in our previous works [5-9]. Working electrodes were prepared from steel specimens with the following composition (mass %): 0.18 C, 0.04 P, 0.05 S, 0.30 Mn, trace Si, and the balance of Fe. The electrodes were prepared by embedding steel rods in an epoxy resin and exposing a surface area of 1 cm<sup>2</sup> to the electrolyte. Prior to each measurement, the sample surfaces were abraded with 400, 600 and 1000 grade emery paper, washed with double-distilled water, degreased with acetone and dried in air.

All electrochemical measurements were conducted in a thermostated conventional threeelectrode Pyrex cell. A saturated calomel electrode (SCE) and a large-area platinum wire were used as the reference and auxiliary electrodes, respectively. The electrolyte was 1 mol L–1 HCl prepared from fuming HCl (Merck Co., Darmstadt – Germany) and double-distilled water. All experiments were performed in 100 mL of electrolytes under non-stirred and naturally aerated conditions maintained at 25 °C.

In all experiments, the carbon steel electrode was allowed to reach the stable open-circuit potential (attained after 1 h). Electrochemical impedance measurements were performed over a frequency range of 100 kHz to 4 mHz at the stable open-circuit potential with an AC wave of 10 mV. The polarization curves obtained after 1 h in the open-circuit potential were collected from the cathodic to the anodic direction from -300 mV below the open-circuit potential to 300 mV above it using a scan rate of  $1.0 \text{ mV} \text{ s}^{-1}$ .

The electrochemical experiments were performed using an Autolab PGSTAT 128 N potentiostat/galvanostat, controlled by GPES/FRA electrochemical software (version 4.9) from Eco-Chemie (The Netherlands).

The inhibition efficiency (n%) was calculated from both the potentiodynamic polarization curves and the electrochemical impedance diagrams, as shown in Eqs. (1) and (2), respectively:

$$n\% = \frac{j_{corr,0} - j_{corr}}{j_{corr,0}} \ x \ 100 \tag{1}$$

where  $j_{corr,0}$  is the corrosion current density in the absence of inhibitor (blank), and  $j_{corr}$  is the corrosion current density in the presence of 100, 200, 300 and 400 mg L<sup>-1</sup> aqueous onion peel extract, as obtained from Tafel plots.

$$n\% = \frac{R_{ct} - R_{ct,0}}{R_{ct}} \times 100$$
<sup>(2)</sup>

where  $R_{ct,0}$  is the charge-transfer resistance in the absence of inhibitor (blank), and  $R_{ct}$  is the charge-transfer resistance in the presence of 100, 200, 300 and 400 mg L<sup>-1</sup> aqueous onion peel extract, as obtained from electrochemical impedance diagrams.

## 2.4. Weight loss experiment

Again the experimental procedure used in the weight loss experiments was very similar to the procedure used in our previous works [5-9]. C-steel specimens with the same composition used in the electrochemical measurements were mechanically cut into  $3.0 \text{ cm} \times 1.0 \text{ cm} \times 1.0 \text{ cm}$  sections, abraded with 100 grade emery paper, sandblasted, washed with double-distilled water, degreased with acetone, and dried in air. Triplicate specimens were immersed in the acid test solutions for 6, 24 and 48 h at 25 °C in the absence and presence of 100, 200, 300, 400 and 1000 mg L<sup>-1</sup> aqueous onion peel extract obtained by infusion. The temperature was controlled using an aqueous thermostat. The specimens were removed, rinsed with water and acetone, dried in warm air and stored in a desiccator. Weight loss was determined by gravimetric tests using an analytical balance with a precision of 0.1 mg. The inhibition efficiency (n%) was obtained using Eq. (3).

$$n\% = \frac{(W_0 - W)}{W_0} x \, 100 \tag{3}$$

where  $W_0$  and W are the corrosion rates (g cm<sup>-2</sup> h<sup>-1</sup>) in the absence (blank) and presence of the extract, respectively.

The temperature effect on the corrosion rate of steel coupons in 1 mol  $L^{-1}$  HCl was examined. These experiments were performed in the absence and presence of 200 mg  $L^{-1}$  aqueous brown onion peel extract with an immersion period of 2 h at 25, 35 and 45 °C.

In the present study, each experiment was repeated three times under the same conditions, and the relative differences between replicate experiments were found to be smaller than 3%, indicating good reproducibility. The average of the three replicated values was used for further processing of the data.

## 2.5. Surface analysis

The specimens used for surface morphology examination were immersed in 1 mol  $L^{-1}$  HCl in the absence (blank) and presence of 400 mg  $L^{-1}$  of aqueous brown onion peel extract at 25 °C for 2 h. The analysis was performed using a Leo 940A (ZEISS) scanning electronic microscope with an accelerating voltage of 20 kV.

#### **3. RESULTS AND DISCUSSION**

#### 3.1. Potentiodynamic polarization curves

The potentiodynamic polarization curves of C-steel in 1 mol  $L^{-1}$  HCl in the absence and presence of aqueous brown onion peel extract in different concentrations are presented in Figure 1. In the presence of the extract there was an inhibition in both anodic and cathodic processes, with a more prominent decrease in the cathodic current densities. This result is typical to the adsorption inhibitors that in this case are the organic compounds present in the brown onion peel extract [7]. These compounds adsorb at the active sites of the metallic surface retarding the metal dissolution (reaction 1) and the hydrogen evolution (reaction 2) slowing the corrosion process described as follows:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-1}$$
 (reaction 1)

 $2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$  (reaction 2)

The open-circuit potential (OCP), corrosion potential ( $E_{corr}$ ), corrosion current density ( $j_{corr}$ ), and the anodic ( $\beta a$ ) and cathodic ( $\beta c$ ) Tafel constants are shown in Table 1. They were obtained by fitting the Tafel plots. It was observed a slight displacement of the  $E_{corr}$  to more cathodic potentials compared to the blank (-26 mV in the presence of 400 mg L<sup>-1</sup> of extract). According to the literature when the difference in  $E_{corr}$  is more than 85 mV with respect to the  $E_{corr}$  of the blank the inhibitor can be classified as cathodic or anodic [7]. Such result indicates that this type of extract acts as a mixed-type inhibitor. There was no significant change in the cathodic ( $\beta c$ ) and anodic ( $\beta a$ ) Tafel slopes in the presence of the extract (Table 1). These results indicate that the adsorbed inhibitor molecules did not

affect both hydrogen evolution reaction and metal dissolution process. An inhibition efficiency of 92.6% was obtained in the presence of 300 mg  $L^{-1}$  of brown onion peel extract.



**Figure 1.** Polarization curves of C-steel in 1 mol  $L^{-1}$  HCl in the absence and presence of varying concentrations of aqueous brown onion peel extract: 100, 200, 300 and 400 mg  $L^{-1}$ .

Table	<b>1.</b> Kir	netic paran	neters obt	ained fro	om the T	Cafel plo	ts for (	C-steel in	1  mol  L	$^{-1}$ HCl in th	e absence
	and p	presence of	aqueous	brown o	nion pee	el extrac	t: 100,	200, 300	) and 400 i	$mg L^{-1}$ .	

[inhibitor]	OCP	E <sub>corr</sub>	jcorr	$\beta_a$	-β <sub>c</sub>	n
$(\text{mg L}^{-1})$	(mV/SCE)	(mV/SCE)	$(mA cm^{-2})$	(mV/dec)	(mV/dec)	(%)
0	-452	-438	0.534	71	126	-
100	-500	-461	0.0496	69	108	90.7
200	-495	-461	0.0433	76	112	91.9
300	-497	-458	0.0394	82	113	92.6
400	-498	-464	0.0420	87	115	92.1

#### 3.2. Electrochemical impendence spectroscopy (EIS)

Figure 2 shows the Nyquist plots of C-steel in a 1 mol  $L^{-1}$  HCl solution in the absence and presence of aqueous brown onion peel extract in different concentrations. Table 2 summarizes the impedance data obtained from the EIS experiments as the charge-transfer resistance ( $R_{ct}$ ) whose value is a measurement of electron transfer across the surface and is inversely proportional to corrosion rate and the double-layer capacitance ( $C_{dl}$ ).

In the absence of the inhibitor (Fig. 2A), only one depressed capacitive loop is observed, which is attributed to the time constant of the charge transfer and the double-layer capacitance. This flatness is due to the nonhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [6]. In the presence of inhibitor (Fig. 2B), the same behavior is observed indicating that the corrosion process even in its presence is controlled by a charge transfer process. The solution resistance ( $R_s$ ) is equal to 1.3  $\Omega$  cm<sup>2</sup> in the absence and presence of the brown onion peel extract.

The double layer capacitance was calculated at the frequency at which the imaginary component of the impedance is maximal  $(f_{max})$  using the equation (4).

$$C_{dl} = \frac{1}{(2\pi f_{maxR_{ct}})} \tag{4}$$

In the absence of the inhibitor it was shown a  $C_{dl}$  value of 646  $\mu$ F cm<sup>-2</sup> and 22  $\Omega$  cm<sup>2</sup>for R<sub>ct</sub>. The R<sub>ct</sub> values increased as the concentration of inhibitor increased. Besides the C<sub>dl</sub> values significantly decreased in the presence of the extract. These results could be explained by a decrease in the active surface area caused by the adsorption of the inhibitors on the carbon steel surface. It suggests that the corrosion process became hindered; this hypothesis is supported by the anodic and cathodic polarization curves results. The best result for the inhibition efficiency was obtained at a concentration of 300 mg L<sup>-1</sup>, with efficiency equal to 94.3%.



Figure 2. Impedance diagrams obtained at the corrosion potential for C-steel in 1 mol  $L^{-1}$  HCl in the absence and presence of aqueous brown onion peel extract: 100, 200, 300 and 400 mg  $L^{-1}$ .

**Table 2.** Electrochemical parameters obtained from the EIS plots for C-steel in 1 mol  $L^{-1}$  HCl in the absence and presence of aqueous brown onion peel extract: 100, 200, 300 and 400 mg  $L^{-1}$ .

[inhibitor] $(mg L^{-1})$	$\frac{R_{ct}}{(\Omega \text{ cm}^2)}$	f <sub>max</sub> (Hz)	$C_{dl}$ (µF cm <sup>-2</sup> )	n (%)
0	22	11.2	646	
100	259	11.2	54.9	91.5
200	280	8.9	63.9	92.1
300	388	5.6	73.2	94.3
400	376	7.1	59.6	94.1

## 3.3. Weight loss measurements

The C-steel corrosion rate ( $W_{corr}$ ) results obtained from weight loss measurements in 1 mol L<sup>-1</sup> HCl in the absence and presence of different concentrations of the inhibitor (100-1000 mg L<sup>-1</sup>) for 6, 24 and 48 h at 25 °C are presented in Table 3.  $W_{corr}$  was greatly reduced with the addition of the extract for all immersion times and was dependent on the extract concentration only in 6 h of immersion. As shown, *n*% increased as the brown onion peel extract concentration increased, varying from 78.2 to 92.2% in the concentration range of 100 to 1000 mg L<sup>-1</sup> for 6 h. Besides it was observed an increase in the inhibition efficiency with time, from 78.2% after 6 h of immersion to 95.9% after 48 h of immersion in the presence of 100 mg L<sup>-1</sup> of extract, which indicates that the inhibition efficiency remains high after long periods of immersion and the adsorption process requires time. The inhibition efficiency reached 96.8% in presence of 400 mg L<sup>-1</sup> after 48 h of immersion.

As it was shown in our previous works [5-9] the discussion of adsorption isotherm behavior using natural product extracts as inhibitors in terms of thermodynamic parameters such as ( $\Delta G_{ads}$ ) is not possible if the molecular mass of the extract components responsible for the adsorption process is unknown. So this study is not present at this time.

	Wcorr $(g \text{ cm}^{-2} \text{ h}^{-1})$	n%	$\frac{\text{Wcorr}}{(\text{g cm}^{-2} \text{ h}^{-1})}$	n %	$\frac{\text{Wcorr}}{(\text{g cm}^{-2} \text{ h}^{-1})}$	n%
Immersion time	6 h		24 h		48 h	
[extract] $(mg L^{-1})$						
0	0.00243		0.00252		0.00221	
100	0.00053	78.2	0.00018	92.9	0.00009	95.9
200	0.00038	84.4	0.00016	93.7	0.00008	96.4
300	0.00036	85.2	0.00014	94.4	0.00008	96.4
400	0.00033	86.4	0.00014	94.4	0.00007	96.8
1000	0.00019	92.2	0.00014	94.4	0.00007	96.8

**Table 3.** C-steel weight loss data for C-steel in 1 mol  $L^{-1}$  HCl in the absence and presence of aqueous brown onion peel extract at the following concentrations: 100, 200, 300, 400 and 1000 mg  $L^{-1}$  for 6, 24 and 48 h at 25 °C.

The influence of temperature on the C-steel corrosion in 1 mol  $L^{-1}$  HCl, from 25 to 45 °C, after 2 h of immersion are presented in Table 4. The experiments were performed in the absence and presence of 200 mg  $L^{-1}$  aqueous brown onion peel extract. The corrosion rates of the C-steel increased as the temperature increased in the absence and presence of the extract, but this increase was higher in the first case.

**Table 1.** C-steel weight loss data in 1 mol  $L^{-1}$  HCl in the absence and presence of 200 mg  $L^{-1}$  of aqueous brown onion peel extract at the following immersion temperatures: 25, 35 and 45 °C, with an immersion period of 2 h.

Temperature	W <sub>corr</sub>	W <sub>corr</sub>	п
(°C)	$(g \text{ cm}^{-2} \text{ h}^{-1})$	$(g \text{ cm}^{-2} \text{ h}^{-1})$	
	Blank	$200 \text{ mg L}^{-1}$	(%)
25	0.002063	0.000869	57.9
35	0.003892	0.001260	67.6
45	0.006570	0.001907	71.0

The apparent activation energy for the corrosion of C-steel in 1 mol  $L^{-1}$  HCl and in inhibited acid solution was determined from an Arrhenius-type plot according to Eq. (5):

$$logW_{corr} = \frac{-E_a}{2.303RT} + logA \tag{5}$$

Where  $W_{corr}$  is the corrosion rate, Ea is the apparent activation energy, A is the frequency factor, T is the absolute temperature, and R is the molar gas constant. Arrhenius plots of (log  $W_{corr}$ ) against (1/T) for C-steel in 1 mol L<sup>-1</sup> HCl, both in the absence and presence of the aqueous brown onion peel extract, are shown in Figure 3. The apparent activation energy obtained for the corrosion process in the free acid solution was found to be 45.7 kJ mol<sup>-1</sup>, and it was found to be 30.9 kJ mol<sup>-1</sup> in the presence of the inhibitor. The energy barrier for the corrosion reaction decreased in the presence of the inhibitor, whereas the inhibition efficiency increased with temperature (Table 4). Such observations can be attributed to the chemisorption of the inhibitor onto the C-steel surface, involving charge sharing or charge transfer from the inhibitor molecules present in the brown onion peel extract to the C-steel surface [7].



**Figure 3.** Arrhenius plots for the corrosion rate of C-steel in 1 mol  $L^{-1}$  HCl solution in the absence and presence of 200 mg  $L^{-1}$  of brown onion peel extract.

## 3.4. Surface analysis

Figure 4 shows a SEM micrograph of C-steel immersed for 2 h in 1 mol  $L^{-1}$  HCl in the absence (Fig. 3A) and presence of 400 mg  $L^{-1}$  of aqueous brown onion peel extract (Fig. 5B) at 25 °C. The morphology in Fig. 3A shows a rough surface due to the uniform corrosion of C-steel in acid, as previously reported [2,5]. In the presence of the aqueous brown onion peel extract (Fig. 3B), the C-steel surface appeared much less corroded, indicating that the surface was protected by an inhibitor film.



**Figure 1.** SEM micrograph (2000x) of C-steel immersed in 1 mol  $L^{-1}$  HCl in the absence (A) and presence of 400 mg  $L^{-1}$  of aqueous brown onion peel extract (B).

3.5. Volatile compounds in aqueous onion extracts by HS-SPME-GC-MS

Volatile compounds in the onion peel extract (Table 5) were consistent with previous reports [32] on onion flavor. As expected, 3(2H)-furanone, 2-hexyl-5-methyl- was the major volatile compound. Hydrocarbons were a major class of volatiles in the extract, with five compounds and 22% of the total chromatographic area. The two sulfur compounds identified are non-polar and formed a minor fraction of the onion peel volatiles (4.71%).

**Table 5.** Volatile compounds in brown onion peel extract by headspace solid-phase microextraction and gas-chromatography mass spectrometry (HS-SPME-GC-MS).

Compounds <sup>a</sup>	RI <sup>b</sup>	Area%
Hydrocarbons		
Dodecane	1112	1.77
Tridecane	1212	2.64
Tetradecane	1310	9.07
Pentadecane	1408	5.20
Heptadecane	1609	3.33
Sulfur compounds		
Disulfide, dipropyl	1103	2.92

1,2-Dithiolane	1150	1.79
Miscellaneous		
3(2H)-Furanone, 2-hexyl-5-methyl-	1541	39.4
5-Octadecyl-pyrimidine-2,4,6-trione	1622	4.97
Propanoic acid	1645	4.15
Benzoic acid, 2-ethylhexyl ester	1717	8.51
Octane, 1,1'-oxybis-	1782	5.74
Total		89.5

<sup>a</sup>Volatile compounds were tentatively identified based on both mass spectra (SI > 90%) and retention index (RI) < 10% difference from published data [33,34]. <sup>b</sup>Experimental RI determined on 5% Phenylmethylpolysiloxane stationary phase.

The other classes of compounds included a furanone, an ester, an ether, a carboxylic acid and a nitrogenous base (pyrimidine). The later, 5-octadecyl-pyrimidine-2,4,6-trione (Figure 5), is amphipathic as it has a hydrophobic hydrocarbon tail and a polar head with two secondary amines. In the acidic medium of corrosion experiments, these two amine groups would be protonated, presenting positive charges, which would increase surface activity of this compound. Surfactants might present corrosion inhibition activity by interaction in the polar metal surface and forming a thin nano-scale non-polar film over the metal plate [35]. 5-Octadecyl-pyrimidine-2,4,6-trione is a plausible candidate for the corrosion inhibition activity presented by the onion peel extract. However, it could not be ruled out that other compounds contributing to the corrosion inhibition activity of onion peel extract were not detectable by headspace GC-MS analysis. Although the headspace-SPME sampling occurred at 60 °C, we also performed analysis by immersion of a new SPME fiber in the extract, and the results (data not shown) were unsatisfactory. In this later analysis, fewer peaks were observed, noise level was higher and the major compounds were identical to those sampled by headspace-SPME. Therefore, other candidates for the corrosion inhibitory activity would have to be non-volatile in the GC-MS injection port, but this hypothesis was not investigated in the present work.



**Figure 5.** Chemical structures of two compounds present in the aqueous brown onion peel extract: the major volatile compound (A) and the plausible candidate for the corrosion inhibition activity presented by the onion peel extract.

## 4. CONCLUSIONS

Aqueous brown onion peel extract showed excellent corrosion inhibition efficiency for C-steel in 1 mol  $L^{-1}$  HCl:

1. All electrochemical results showed that the aqueous brown onion peel extract acted as adsorption inhibitor on the C-steel surface with predominantly cathodic characteristics.

2. The inhibition efficiency of C-steel corrosion in 1 mol  $L^{-1}$  HCl increased significantly with the extract concentration only in low immersion time.

3. The inhibition efficiency of C-steel corrosion in 1 mol  $L^{-1}$  HCl increased with temperature and consequently the Ea of the C-steel corrosion process decreased in the presence of the extract. This result can be attributed to a strong chemisorption of the inhibitor onto the steel surface, involving charge sharing or charge transfer from the inhibitor molecules present in the brown onion peel extract to the C-steel surface.

4. HS-SPME assays of the extract showed few volatile compounds with 3(2H)-Furanone, 2-hexyl-5-methyl- as the major volatile compound and a nitrogenous base (5-octadecyl-pyrimidine-2,4,6-trione) which may play an important role in the inhibition process.

5. SEM analysis showed that the C-steel surface is protected by the presence of the brown onion peel extract.

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## References

- 1. A.K.Satapathy, G. Gunasekaran, S.C. Sahoo, A. Kumar and P.V. Rodrigues, *Corros. Sci.*, 51 (2009) 2848.
- 2. V.V. Torres, V.A. Rayol, M. Magalhães, C.M. Viana, L.C.S. Aguiar, S.P. Machado, H. Orofino and E. D'Elia, *Corros. Sci.*, 79 (2014) 108.
- 3. K. Shalabi1, Y.M. Abdallah, Hala M. Hassan, A.S. Fouda, *Int. J. Electrochem. Sci.*, 9 (2014) 1468.
- 4. P.B. Raja and M.G. Sethuraman, Mater. Lett, 62 (2008) 113.
- 5. S.S.A.A. Pereira, M.M. Pegas, T.L. Fernandez, M. Magalhães, T. G. Schontag, D C. Lago, L F.de Senna and E. D'Elia, *Corros. Sci.*, 65 (2012) 360.
- 6. J.C. da Rocha, J.A C.P. Gomes and E. D'Elia, Corros. Sci., 52 (2010) 2341.
- 7. V.V. Torres, R.S. Amado, C.F. de Sá, T.L. Fernandez, C.A.S. Riehl, A.G. Torres and E. D'Elia, *Corros. Sci.*, 53 (2011) 2385.
- 8. J.C. da Rocha, J.A.C. P. Gomes, E. D'Elia, A.P.G. Cruz, L.M.C. Cabral, A.G. Torres and M.V.C. Monteiro, *Int. J. Electrochem. Sci.*, 7 (2012) 11941.
- 9. T. F. Souza, M. Magalhães, V.V. Torres and E. D'Elia, Int. J. Electrochem. Sci., 10 (2015) 22.
- 10. K.M. Emran, N.M. Ahmed, B.A. Torjoman, A.A. Al-Ahmadiand S.N. Sheekh , *J. Mater. Environ. Sci.*, 5 (2014) 1940.
- 11. I.E. Uwah, P.C. Okafor and V.E. Ebiekpe, Arabian J. Chem., 6 (2013) 285.
- 12. O.K. Abiola, J.O.E. Otaigbeand O.J. Kio, Corros. Sci., 51 (2009) 1879.
- 13. T. Ibrahim and M. Habbab, Int. J. Electrochem. Sci., 6 (2011) 5357.

- 14. O.K. Abiolaand J.O.E. Otaigbe, Corros. Sci., 51 (2009) 2790.
- M.A. Quraishi, A. Singh, V.K. Singh, D.K. Yadavand A.K. Singh, *Mater. Chem. Phys.*, 122 (2010) 114.
- 16. M.H. Hussin and M.J. Kassim, Mater. Chem. Phys., 125 (2011) 461.
- P. Kalaiselvi, S. Chellammal, S. Palanichamyand G. Subramanian, *Mater. Chem. Phys.*, 120 (2010) 643.
- 18. A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady and M. Saadawy, *Corros. Sci.*, 48 (2006) 2765.
- 19. A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit and P.V. Rodrigues, *Corros. Sci.*, 51 (2009) 2848.
- 20. A. Bouyanzer, B. Hammouti and L. Majidi, Mater. Lett., 60 (2006) 2840.
- 21. L.R. Chauhan and G. Gunasekaran, Corros. Sci., 49 (2007) 1143.
- 22. M. Sangeetha, S. Rajendran, J. Sathiyabam and P. Prabhakar, *J. Nat. Prod. Plant Resour.*, 2 (2012) 601.
- 23. T.H. Ibrahim, Y. Chehade and M.A. Zour, Int J. Electrochem. Sci., 6 (2011) 6542.
- 24. A. Y. El-Etre, Appl. Surf. Sci., 252 (2006) 8521.
- 25. A. Y. El-Etre, Mater. Chem. Phys., 108 (2008) 278.
- 26. P.C. Okafor, V I. Osabor, E.E. Ebensoand Pigm.Res.Technol., 36 (2007) 299.
- A.J. Almaraj, J.W. Sahayaraj, A.P.P. Regis, A. Sahayaraj, P. Pandian, P. Johnrai, A. Kasthuri and C. Kumar, *Engineering*, 5 (2013) 178.
- 28. N.J.N. Nnaji, C.O.B. Okoye, N.O. Obi-Egbedit, M.A. Ezeokonkwo and J.U. Am, *Int. J. Electrochem. Sci.*, 8 (2013) 1735.
- 29. S. Sulaiman, A. Nor-Anuar, A. S. Abd-Razak and S. Chelliapan, Res. J. Chem. Sci., 2 (2012) 10.
- 30. K.S. Parikh and K.J. Joshi, *Trans SAEST*, 39 (2004) 29.
- 31. J. Dai and R.J. Mumper, Molecules, 15 (2010) 7313.
- 32. N.C.J.P. Lekshmi, S. Viveka, M.B. Viswanathan, G. Manivannan and T.M. Shobi, *Nanobio Pharmaceutical Technology*, Anna University, Tamil Nadu (2014).
- 33. M. Kuo and C. Ho, J. Agric. Food Chem., 40 (1992) 1906.
- C. Colina-Coca, D. González-Peña, E. Vega, B. de Ancos, C. Sánchez-Moreno, *Talanta*, 103 (2013) 137.
- M.A. Malik, M.A. Hashim, F. Nabi, S.A. AL-Thabaiti and Z. Khan, Int. J. Electrochem. Sci., 6 (2011) 1927.

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