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Corrosion Inhibition of Mild Steel in 15 wt.% HCl by Durum Wheat

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Abstract

The toxicity of most commercial corrosion inhibitors and strict environmental legislations have required the development of environmentally-friendly, cheap and non-toxic inhibitors. The use of natural products, especially of plant origin as corrosion inhibitors has become an area of increasing research because plant extracts contain an incredibly rich source of natural chemical compounds which can be extracted by simple procedures at low-cost. Durum wheat was investigated in this work because functional groups were identified which suggested that it could be a promising potential inhibitor.

The corrosion of mild steel in 15 wt.% HCl solution with and without Durum wheat was investigated and directly compared to results from two commercial corrosion inhibitors, propargyl alcohol and 2- mercaptobenzimidazole, under the same conditions, by comparing weight loss with and without inhibition. The durum wheat powder and adsorbed films were characterised by Fourier transform infrared spectroscopy (FTIR), and the exposed samples were characterised using SEM, EDS spectroscopy and surface profilometry. The effects of concentration, temperature (20-60°C) and immersion time (5-24 h) on the corrosion inhibition were investigated.

Durum wheat was shown to be a successful green corrosion inhibitor with a room temperature inhibition efficiency of 97% (as compared to values of 99% and 97% for propargyl alcohol and 2 - mercapto benzimidazole respectively) and at a lower cost per l L of corrosive solution. However, at the severe corrosive conditions chosen for this research, the inhibition performance of both durum wheat and 2- mercaptobenzimidazole was influenced by time and temperature, and the durum wheat corrosion inhibition was reduced to 78% after 24 hours at 60°C, compared to 88% for 2- mercaptobenzimidazole. All the inhibitors investigated obeyed Langmuir adsorption isotherm.

Keywords corrosion inhibition; plant extracts; adsorption isotherm; mild steel; acid solution

Introduction
Mild steel is widely used for several applications because of its low cost and good properties such as ductility, malleability, weldability and machinability. However, it is highly corroded when exposed to aggressive environments like acidic solutions during industrial processes (acid pickling, acid storage, oil well stimulation, acid descaling and industrial acid cleaning)[1]. Hydrochloric acid (HCl) is commonly used in several industrial applications (as mentioned above) because it forms metal chlorides that are highly soluble in aqueous phase compared to other mineral acids [2]. Generally, inhibitors are added to corrosive solutions to reduce metal dissolution and acid consumption. The use of inhibitors has proven to be practical, efficient and economical [3]. According to Umoren et al.[4], the general pre-requisite for the selection of suitable inhibitors are as follows: the ability of the inhibitor molecules to oxidize metal(s), the presence of heteroatoms (S, N and O) in their functional groups that can donate unshared electrons to the 3-d orbitals of Fe atoms, the ability to cover large surface areas of the metal with stable adsorbed film, solubility in the aqueous solution(s), possession of pi-electrons, non-toxic and cheap.

Synthetic organic compounds have been reported in the literature to be effective in mitigating corrosion, but because they are highly toxic and do not satisfy Environmental, Health and Safety regulations, it is necessary to find green alternatives. These negative effects have led to increasing interest in the development of natural products (e.g plant extracts) because of their availability, low cost, simple extraction procedures, biodegradability and low toxicity. The abundance of phytochemicals in plant extracts such as alkaloids, phenols, tannin, flavonoids, saponins etc. has motivated industries and academia to explore their corrosion inhibitive properties. Some of these plant extracts are: Geissospermum [5], marigold flower [6], musa paradisiac [7], phyllanthus amarus[8], artemisa pallens [9], aloe vera [10], garlic [11], ginkgo[12], osmanthus fragran [13], neolamarkia cadamba [14], justicia gendarussa [15], henna [16], and zenthoxylum alatum [17].

Durum wheat (DW) is a monocotyledon plant of the Gramineae family that belongs to the genus Triticum. It is mostly grown in the Mediterranean area and commonly used for pasta production, semolina, couscous and bulgur [18]. Kamil et al. [19] reported -NH stretching of protein, amide I (C=O) [19], amide II (C-N) and C-O-C stretching of starch in DW molecules. These identified functional groups in DW is the rationale for its investigation as a possible candidate inhibitor. In this work, the inhibitive performance of DW on the corrosion of mild steel in 15 wt.% HCl was investigated by weight loss measurement and compared with commercially available inhibitors (propargyl alcohol and 2-mercapto benzimidazole). Also, surface analytical measurements were done via scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS).

Materials
Mild steel specimens
Mild steel (MS) sheet was cut to size 60 mm × 40 mm × 3mm. The samples were degreased with acetone, thoroughly washed with distilled water and dried by a hot air stream. Then, the back and edges of the samples were sealed with lacquer (Indestructible paint, U.K.) to prevent initiation of corrosion at the edges. After which the samples were weighed on an electronic balance (Sartorius PRACTUM 213-1S, Germany) with a precision of ± 0.01 mg and stored in a desiccator. The chemical composition of the mild steel sample is shown in Table 1.

Element	C	Mn	S	P	Cu	Ni	Al	Cr	Si	Fe
Composition (wt.%)	0.06	0.32	0.02	0.01	0.02	0.02	0.005	0.03	0.01	balance

Inhibitor preparation

Propargyl alcohol , PA, (99% purity) and 2-mercaptobenzimidazole, 2-MI, (98% purity) were procured from Sigma -Aldrich (Dorset, U.K.) and used without further purification. Durum wheat was obtained in powder form from east end foods (Nottingham, U.K.). The inhibitors were used by adding 1, 4, 7 and 10g in 595 ml distilled water, stirred and made up to 1000 ml with 37 wt. % HCl.

Electrolyte

The test solution (15 wt.% HCl) was prepared by diluting analytical reagent (AR) 37 wt.% HCl (ThermoFisher Scientific, U.K.) with distilled water. For each of the experiments, fresh solution of test solution was prepared.

Methods

Immersion test

The prepared and weighed samples were immersed in 5 L beakers containing 3000 mL of 15 wt.% HCl (which were all placed in a water bath) in the absence and presence of different concentrations of the inhibitors at 20, 40 and 60 $\pm$ 2$°C$. The temperatures were monitored with a K- type thermocouple by inserting its probe into the electrolyte(s). After the immersion time elapsed, the samples were removed from the solutions, thoroughly washed with running water, dried with a hot air stream and re- weighed using an electronic balance. The studied immersion times was between 5 h and 24 h. Three samples were immersed in each beaker, and to check reproducibility, some of the corrosion experiments were repeated under identical conditions.

The corrosion rate (C_R) was calculated using the following equation [3, 12, 16]:

$$CR=\left(\frac{\Delta W}{A \times t}\right) \tag{1}$$

where ΔW is the average weight loss, A is the total surface area of the sample, and t is the exposure time.

The inhibition efficiency (η) was calculated from the corrosion rate values as follows [3, 12, 16]:

$$IE \ (\%)=\left(\frac{C_R^0-C_R^i}{C_R^O}\right) \times 100 \tag{2}$$

Surface analysis

MS samples were immersed in 15 wt. % HCl in the absence and presence of 7 g/l PA, 2-MI and DW at 60°C. After 5 h, the samples were taken out from the solutions, thoroughly washed with distilled water and dried with hot air stream. Then, the surface morphology of the MS samples was examined using Philips XL 30 SEM with an electron beam of 20 kV and a working distance of 10 mm.

Energy dispersive X-ray spectroscopy (EDS) was used to determine the elemental composition of the MS samples via Philips XL 30 SEM-EDS. The data were collected at three different areas and processed with Oxford INCA software.

Surface profilometry
Surface roughness measurements of the uninhibited and inhibited MS surfaces were carried out using a Bruker NPFLEX profilometer (non-destructive and non-contact) with a vertical resolution of <0.15 nm and 5× objectives. The analysed sample area was 1260 µm × 940 µm and the data was analysed with a Bruker Vision 64 software.

Fourier transform infrared spectroscopy
The as-received PA, 2-MI and DW were placed on attenuated total reflectance (ATR) crystal and then the crank was gently turned down to press the sample onto the crystal surface for good contact. The background and sample times were average of 64 scans. All spectra were obtained at a resolution of 4 cm^{-1} in the wavenumber range of 4000-500 cm^{-1} via a Bruker Tensor FTIR spectrometer coupled with ATR accessory.

Results
Fourier transform infrared spectroscopy (FTIR) of the as received DW powder was used to examine what functional groups were present in the DW powder. Fig. 1 shows the FTIR spectrum of DW powder. The strong and broad peak at 3287 cm^{-1} is assigned to the presence of NH stretching vibration of protein. The two peaks at 2925 and 2855 cm-1 are attributed to CH stretching [20]. The absorption band at 1646 cm^{-1} corresponds to the stretching vibration of C=O (amide I). The amide II (-CN and- NH bending) is observed at a peak at 1541 cm^{-1}[20]. The peak at 1077 cm^{-1} is assigned to the presence of C-C stretching [19, 20]. The last two peaks at 996 and 757 cm^{-1} are attributed to C-O stretching and out –of- phase C- H bending band in the aromatic ring [21].
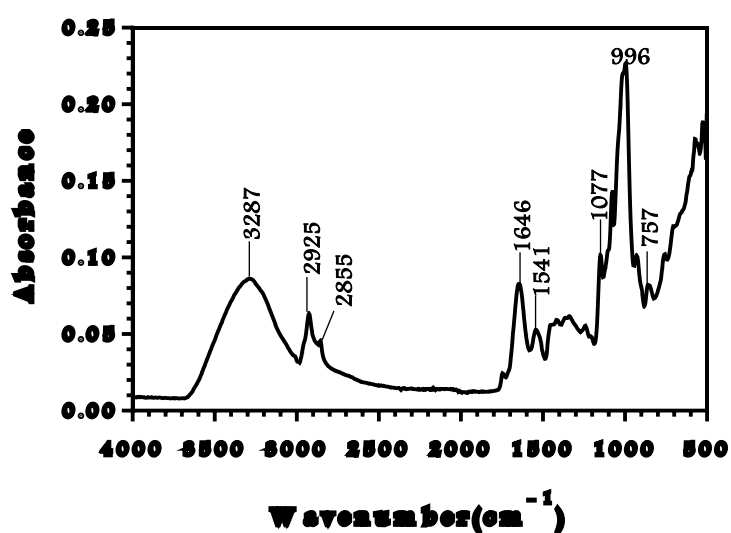

Figure 1. FTIR spectrum of durum wheat (DW).

Fig. 2 shows the FTIR spectrum of PA molecule. The peak at 3290 cm^{-1} can be assigned to the presence $\equiv$C-H stretching. The peaks that appeared at 2931 and 2875 cm^{-1} are attributed to CH$_2$ stretching vibration. The presence of C$\equiv$C was observed at a peak of 2121 cm^{-1}. The peak at 1424 cm^{-1} is due to the presence of CH$_2$ vibration. The peaks at 1024 and 638 cm^{-1} are assigned to C-O stretching and $\equiv$C-H vibration, respectively [22].

The FTIR spectrum of 2-MI is shown in Fig. 3. The peak at 3148 cm^{-1} is assigned to the presence of N-H stretching. The peak at 2569 cm^{-1} is attributed to S-H vibration. The N- C- S- N vibration is observed at a peak of 1618 cm^{-1}. The peak at 1462 cm^{-1} is due to the presence of C- N vibration. The peaks at 1015 and 696 cm^{-1} are attributed to the presence of N-C=S and C- S vibrations, respectively[23].
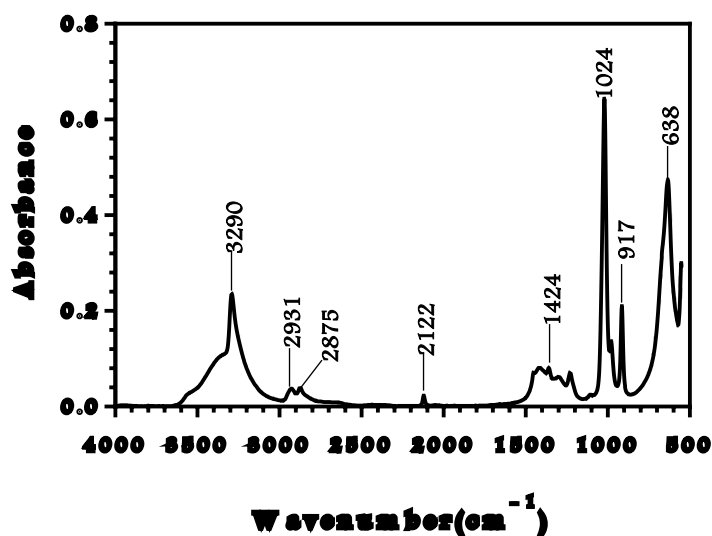

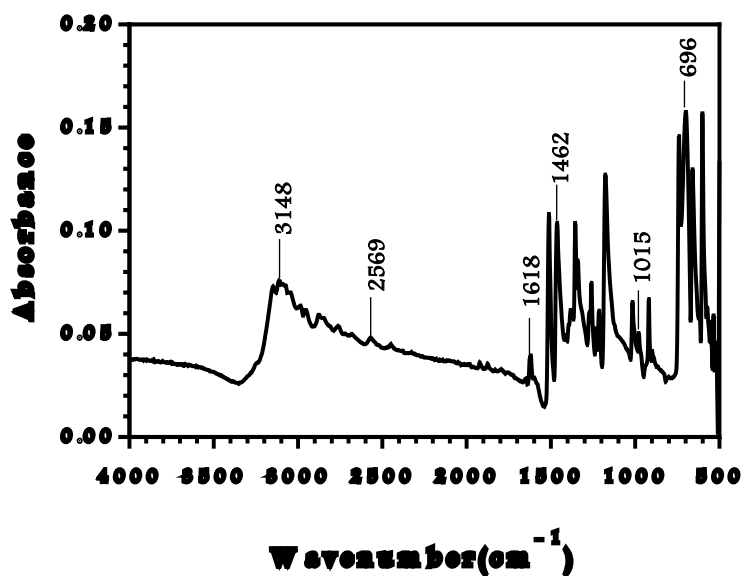*Figure 2. FTIR spectrum of propargyl alcohol (PA).*

Figure 3. FTIR spectrum of 2-mercaptobenzimidazole (2-MI).

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<u>Weight loss measurements</u>

The values of corrosion rates and inhibition efficiencies obtained from weight loss measurements for various concentrations of PA, 2-MI and DW in 15 wt.% HCl at 20°C for 5 h are presented in Fig. 4 and Table 2. As can be seen, the corrosion rates decreased and inhibition efficiencies increased with increasing concentration of all inhibitors. This implies that more inhibitor molecules adsorbed onto MS surfaces with increasing inhibitor concentration. The maximum inhibition efficiencies of 99.66%, 96.50% and 97.40 % were obtained at 7 g/l for PA, 2-MI and DW respectively. Further increase of the concentration beyond 7g/l does not change their inhibitive performance. This could be due to aggregation of the inhibitor molecules at metal/solution interface, hence forming micelles that blocked the corrosion sites [24, 25]. The inhibition efficiencies of the studied inhibitors follow this order: PA>DW>2-MI at 20ºC for 5 h. The inhibition efficiency of propargyl alcohol has been reported to be over 99% [22].
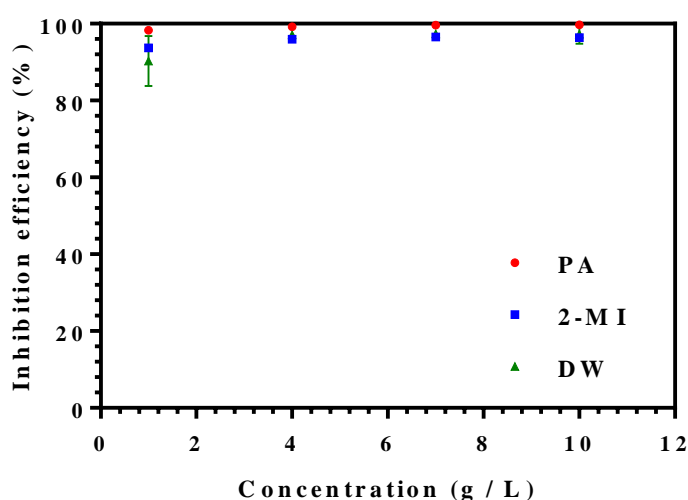

Figure 4. Effect of concentration on the inhibition efficiency
of different concentrations of PA, 2-MI and DW at 20°C for 5 h.
Error bars represents ± 1 SD.

Table 2. Corrosion parameters obtained from immersion test for MS in 15 wt.% HCl in the absence and presence of different concentrations of the inhibitors at 20°C for 5 h. Error bars represents ± 1 SD.

Inhibitor	Concentration (g l^{-1})	CR (mg cm^{-2} h^{-1})
Blank	0.0	2.702 ± 0.040
PA	1.0	0.047 ± 0.001
	4.0	0.020 ± 0.012
	7.0	0.009 ± 0.006
	10.0	0.009 ± 0.004
2-MI	1.0	0.171 ± 0.025
	4.0	0.109 ± 0.021
	7.0	0.095 ± 0.010
	10.0	0.098 ± 0.004
DW	1.0	0.262 ± 0.174
	4.0	0.078 ± 0.019
	7.0	0.070 ± 0.009
	10.0	0.073 ± 0.069

Fig. 5 shows the effect of immersion time on the inhibition performance of the inhibitors for MS in 15 wt.% HCl at 60ºC for 5, 10 and 24 h with optimum concentration of 7 g/l (PA, 2-MI and DW). The inhibition efficiency of PA remained unchanged with increasing immersion time. These values are over 99%, suggesting strong adsorption of the inhibitor on mild steel. The inhibition efficiency of 2- MI also remained approximately constant. However, the inhibition efficiency of the green inhibitor (DW) decreased with increasing immersion time. The inhibition efficiencies of DW were 87.46 ± 0.25 %, 82.17 ± 0.53 % and 77.64 ± 0.29 % at 5, 10 and 24 h respectively.

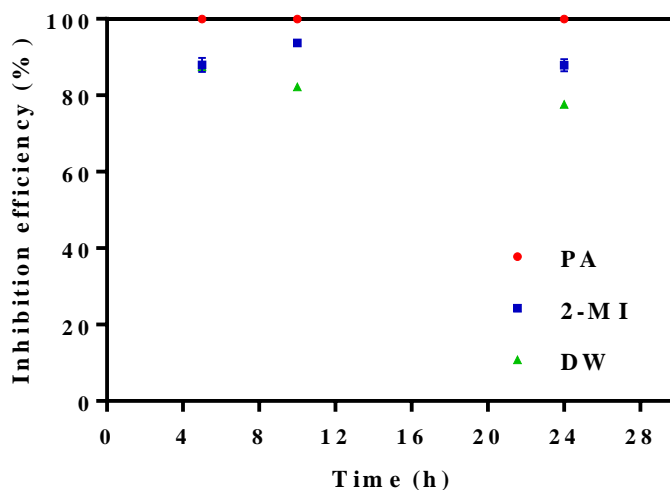*Figure 5. Effect of time on the inhibition efficiency of PA, 2-MI and DW for MS in 15 wt.% HCl at 5, 10 and 24 h. Error bars represents ± 1 SD.*

Fig. 6 shows the results for the inhibition efficiency of PA as a function of temperature for 5 h. It can be seen that the corrosion inhibition performance of PA remained unchanged (over 99%) with increasing temperature. Podobaev and Avdeev [26] attributed the high inhibition

efficiency (over 99%) of propargyl alcohol to the formation of thick protective polymer films at metal/HCl interface. On the hand, the inhibition performance of 2-mercaptobenzimidazole and durum wheat (green inhibitor) decreases with increasing temperature. This may be due to the desorption of the inhibitor molecules from MS surface with increasing temperature [27]. At 60°C, the inhibition efficiencies of 2-MI and DW are 87.99 ± 1.86 % and 87.46 ± 0.25 %, respectively. As it can be seen, the performance of DW matches with 2-MI (87%) at 60°C.

Figure 6. Variation of inhibition efficiency with temperature for mild steel in 15 wt.% HCl containing 7 g/l (optimum concentration) of PA, 2-MI and DW for 5 h. Error bars represent ±1 SD.

Fig. 7 shows the effect of temperature on the inhibition effiency of PA, 2-MI and DW for mild steel in 15 wt. % HCl at 20, 40 and 60°C for 10 h. It can be clearly seen that all the studied inhibitors are stable in the temperature range tested. However, PA and 2-MI outperformed DW in these conditions. At the highest temperature (60°C), the inhibition efficiencies of PA, 2-MI and DW are 99.95 ± 0.04%, 93.75 ± 0.50 % and 82.17 ± 0.53 %, respectively.
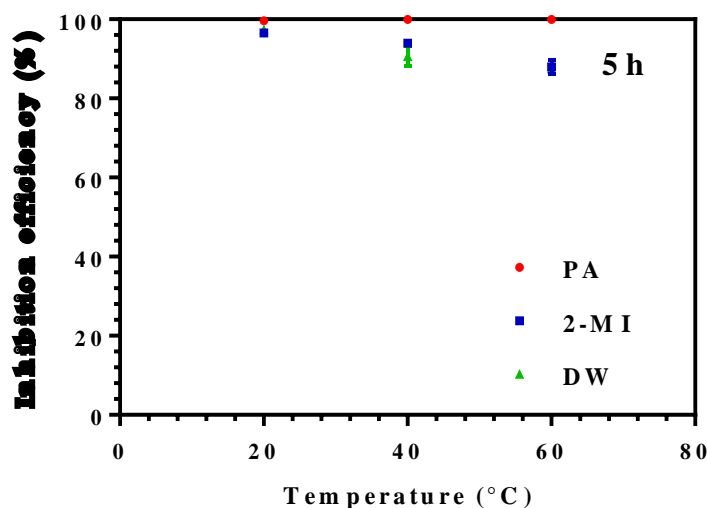

Figure 7. Variation of inhibition efficiency with temperature for mild steel in 15 wt.% HCl containing 7 g/l (optimum concentration) of PA, 2-MI and DW for 10 h. Error bars represent ±1 SD.

Fig. 8 shows the effect of temperature on the inhibition efficiency of PA, 2-MI and DW at 20, 40 and 60°C after 24 h immersion time. It was found that the inhibition efficiency of PA molecule was stable with increasing temperature for 24 h (over 99%). This further confirmed the strong inhibitive action of PA molecule in HCl solution, which is attributed again to the formation of strong polymeric films on MS surface [22]. However, the inhibition efficiency of 2-MI and DW decreased with temperature after 24 h. The inhibition efficiencies of PA, 2-MI and DW are 99.93 ± 0.02 %, 87.87 ± 1.55 % and 77.64 ± 0.29 %, respectively at 60°C for 24 h immersion.
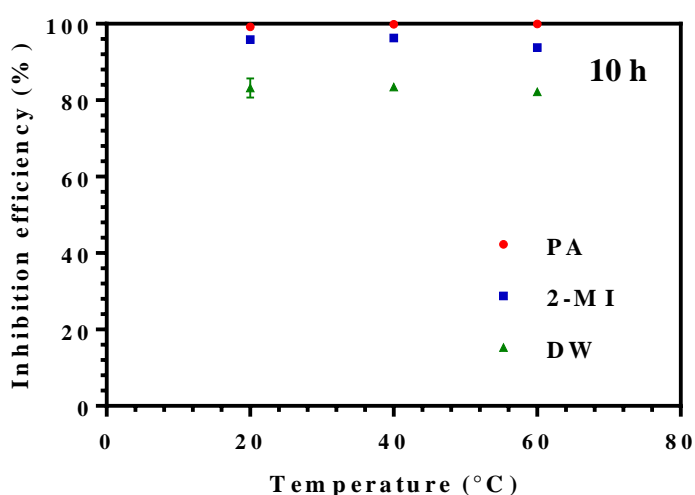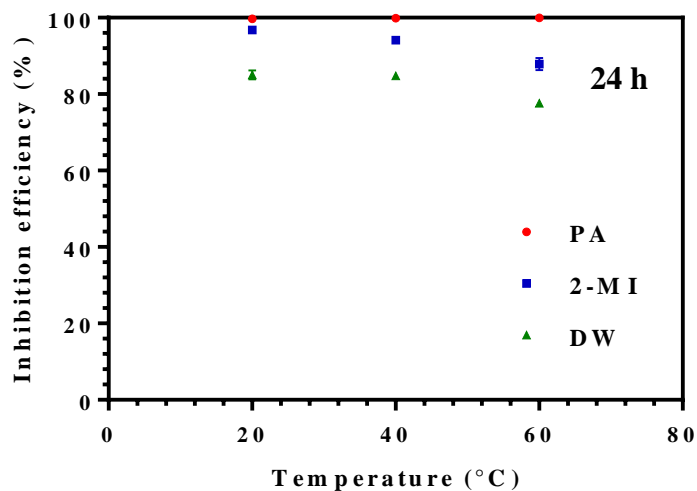

Figure 8. Variation of inhibition efficiency with temperature for mild steel in 15 wt.% HCl containing 7 g/l (optimum concentration) of PA, 2-MI and DW for 24 h. Error bars represent ± 1 SD.

SEM analysis

Fig. 9 A shows a highly corroded and rough surface of MS in the absence of the inhibitor. However, the surfaces of MS treated with the inhibitors (depicted in Figs. 9B, C and D) were less corroded and smoother as a result of the inhibitors. This suggests that the MS surfaces were modified in the presence of the inhibitors. Also, it can be seen that the surface of MS treated with PA was the smoothest.
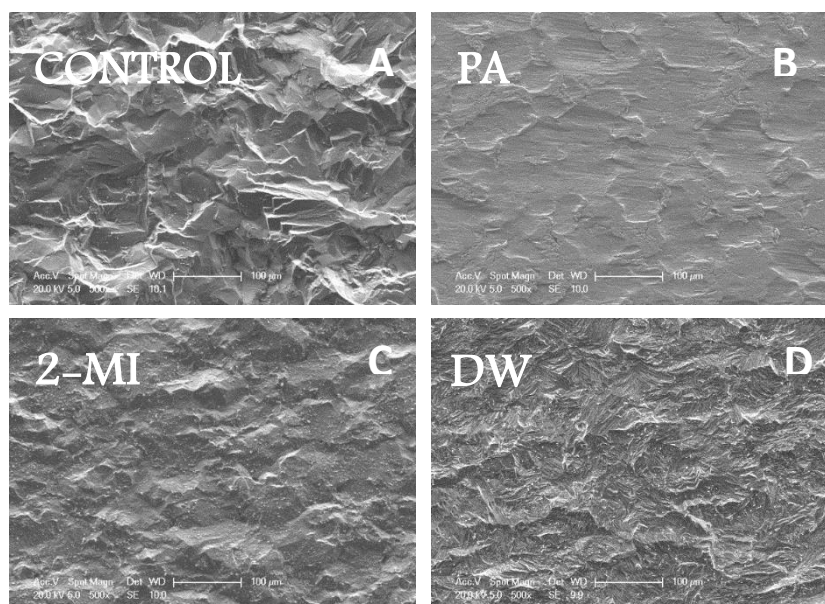

Figure 9 SEM micrographs of MS surfaces immersed in 15 wt.% HCl. A. no inhibitor B. 7 g/l propargyl alcohol C. 7 g/l 2-mercaptobenzimidazole D. 7 g/l durum wheat at 60ºC for 5 h.

The EDS analysis results of MS surfaces in 15 wt.% HCl in the absence and presence of 7 g/l PA, 2- MI and DW at 60°C for 5 h is presented in Table 3. The EDS analysis results of MS in the absence of inhibitor shows a highly oxidised surface with a significant amount of O (13.94 wt.%) and also chlorine (0.84%). This can be confirmed with a highly corroded and rough surface (Fig. 4a). On the other hand, there was less O on MS surface treated with the inhibitors. Also, it can be seen that no Cl was present on surfaces of MS treated with PA and DW. These results reveal that the surfaces of MS were improved in the presence of the inhibitors and reduce the attack of the corrosive medium as compared to inhibitor-free MS surface, which is highly oxidised.

Table 3 EDS analysis results of MS immersed in 15 wt.% HCl in the absence and presence of 7 g/l inhibitors at 60°C for 5 h. Error bars represent ± 1 SD.

Medium	Elemental composition (wt.%)			
	Fe	C	O	Cl
Blank	69.99 ± 2.76	15.23 ± 2.25	13.94 ± 3.44	0.84 ± 0.28
MS with PA	82.79 ± 1.00	15.99 ± 0.09	1.22 ± 1.06	-
MS with 2-MI	84.88 ± 0.87	8.28 ± 0.58	6.46 ± 1.22	0.34 ± 0.15
MS with DW	90.29 ± 0.30	7.40 ± 0.44	2.39 ± 0.01	-

Surface profilometry

The surface roughness of the as-received samples was measured to be 1.35 ± 0.15 µm (n=3) Table 4 shows the average surface roughness of uninhibited and inhibited MS surfaces in 15 wt.% HCl at 60ºC for 5 h. It can be clearly seen from the data that the surface roughness of MS in uninhibited solution (blank) was higher than that in the inhibited solution. These results show that the attack of the corrosive solution on MS was reduced in the presence of optimum concentration of all the studied inhibitors. Also, the average roughness value of MS surface treated with PA was the lowest compared to those treated with 2-MI and DW.

Table 4 Average surface roughness of MS in 15 wt.% HCl without and with 7 g/l of the studied inhibitors at 60ºC for 5 h. Error bars represent ± 1 SD.

Medium	Blank	PA	2-MI	DW
Surface roughness (Sa)	3.69 ± 0.29	1.26 ± 0.04	3.11 ± 0.19	1.93 ± 0.15

Adsorption isotherm

The adsorption isotherm parameters help to understand the interaction between corrosion inhibitors and MS surface. The adsorption mechanisms of the studied inhibitor molecules onto MS were investigated by fitting the surface coverage (θ) values obtained from the calculated inhibition efficiencies into Langmuir, Temkin, Flory-Huggins and Freundlich isotherms. Langmuir isotherm gave the best fit with values of correlation coefficients (R^2) and slopes near unity. The Langmuir isotherm model is given by the following equation [12]:

$$\text{Langmuir isotherm:} \quad \frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{3}$$

where C is the inhibitor concentration in the bulk solution, K_{ads} represents the adsorption equilibrium constant and θ ($\eta/100$) represents the fraction of the metal surface covered by the inhibitor.

The adsorption equilibrium constant (K_{ads}) is related to the free energy of adsorption (ΔG_{ads}) by the equation[12]:

$$\Delta G^{\circ}_{ads} = - RT \ln (C_w K_{ads}) \tag{4}$$

where C_w is the concentration of water (1000 g /L), R is the universal gas constant, and T is the absolute temperature. The unit of C_w is expressed in 1000 g/L instead of 55.5 mol L^{-1} for consistency with K_{ads} units (L g^{-1}). The adsorption equilibrium constant is obtained from the reciprocal of the intercepts from the straight lines on the C/θ axis.

Fig. 10 shows the Langmuir isotherm plots of C/θ against C for the adsorption of different concentrations of PA, 2-MI and DW molecules on MS surfaces at 20, 40 and 60°C for 5 h. The values of linear correlation coefficient close to 1 (Table 5) suggest that the adsorption of the studied inhibitors follows Langmuir isotherm model. Generally, values of ΔG_{ads} up to -20 kJ/mol are attributed to the electrostatic interaction between the inhibitor molecules and the metal surface (physical adsorption), whilst those at -40 kJ/mol or more negative are consistent with chemical bonding of the inhibitor to the sample (Chemisorption) [12]. The values between 20 and 40 kJ/mol suggest mixed adsorption (i.e. physical and chemical). As shown in Table5, the calculated values of ΔG_{ads} suggest that PA and DW molecules adsorbed on MS /solution

interface by both physical and chemical mode from 20-60°C. Between 20 and 40°C, the values of ΔG_{ads} from -25.33 to -26.80 kJ mol^{-1} indicates both physical and chemical adsorption of 2-MI on MS surface.The lower value of ΔG_{ads} at 60°C (-18.39 kJ mol^{-1}) indicate that the mechanism may be moving towards only physisorption. In physical adsorption, the interaction between the inhibitor molecules and the substrate is due to Van der Waals forces, which is weak and reversible.

Table 5. Adsorption parameters for the corrosion of MS in 15 wt.% HCl containing 7g/l PA, 2-MI and DW at different temperatures for 5 h.

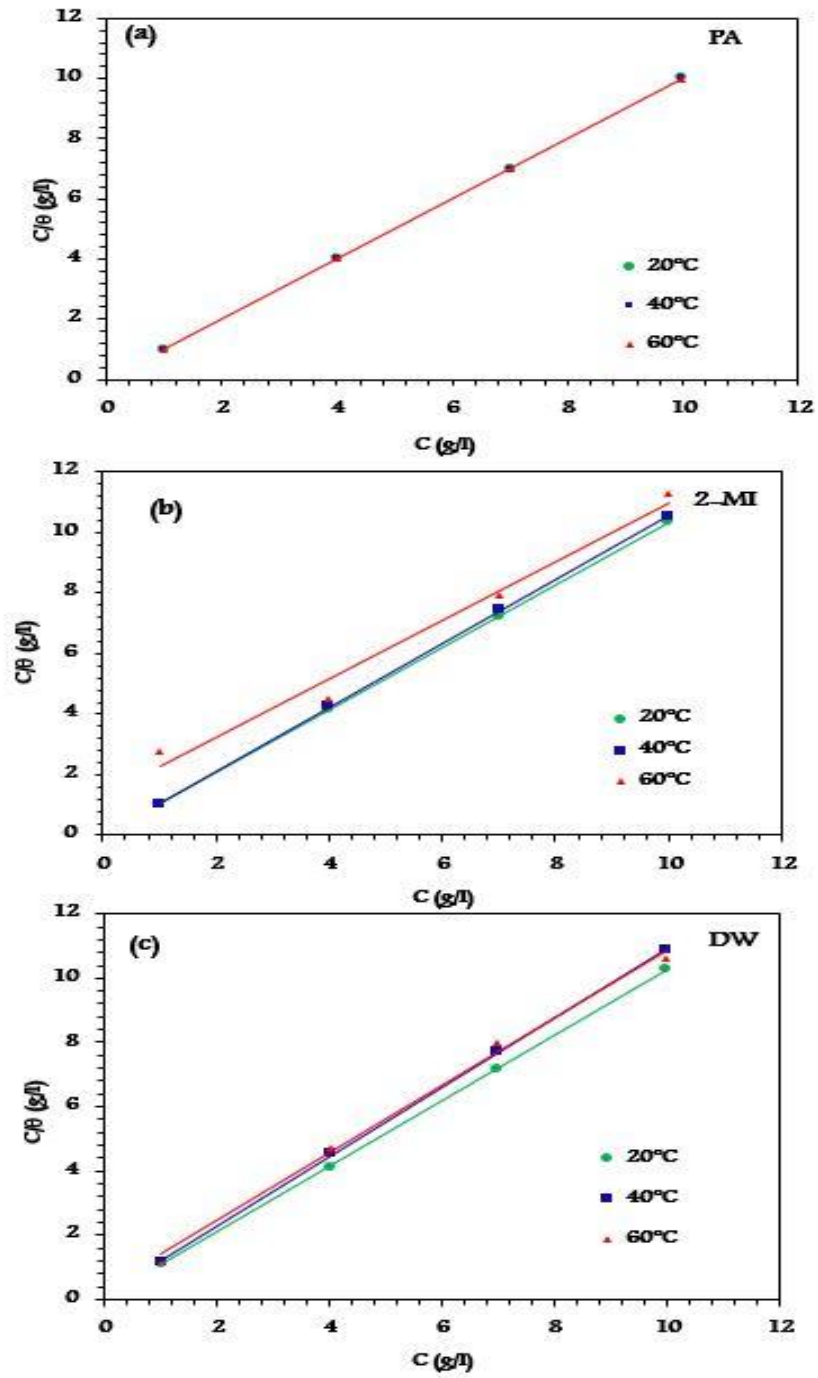| Inhibitor	Temperature (K)	Correlation coefficient (r^2)	K_{ads} (L g^{-1})	$-\Delta G_{ads}$ (kJ mol^{-1})
PA	293	0.9999	51.23	26.42
	313	0.9999	535.62	34.33
	333	0.9999	193.55	33.70
2-MI	293	0.9999	32.79	25.33
	313	0.9999	29.67	26.80
	333	0.9820	0.77	18.39
DW	293	0.9999	15.27	23.47
	313	0.9997	2.31	20.16
	333	0.9958	2.92	22.09

Figure 10. Langmuir adsorption plots of (a) PA, (b) 2-MI and (c) DW for MS in 15 wt.% HCl at 20, 40 and 60 °C for 5 h.

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Discussion

The results from this study show that durum wheat can act as a green corrosion inhibitor for mild steel in 15 wt. % HCl solution in the range of conditions investigated. As it can be seen from Fig. 4, the same concentration of commercial inhibitors (propargyl alcohol and 2- mercapto benzimidazole) and durum wheat is required to achieve optimum performance. At low temperature (20°C), durum wheat performed better than 2- mercapto benzimidazole at the same optimal concentration with inhibition efficiency of 97%, but propargyl alcohol was the most effective (Figure 4).

The acidic concentration chosen for this work is fairly extreme, leading to large corrosion rates (if no inhibitor is present Table 2) and rough surfaces (Fig. 9). The performance of durum wheat slightly dropped with different time of immersion (5- 24 h) and temperature (20- 60°C), see Figs. 5-8, which is consistent with previous reports of other plant inhibitors [3, 16, 28, 29]. This behaviour may be due to desorption of inhibitor molecules from mild steel surface or degradation with time. Similar behaviour has been reported in the literature for most green corrosion inhibitors [30]. Even with the influence of time and temperature, the corrosion inhibition efficiency of DW is still over 77% at 60°C for 24 h.

The high inhibition performance of propargyl alcohol with immersion times and temperatures could be attributed to the formation of polymeric films on the surface of MS. Also, triple bond and hydroxyl group of propargyl alcohol molecule are considered the active adsorption centres for the adsorption of the molecules onto the metal surface. Pooling et al. [22] reported that the thicker polymeric film formed by propargyl alcohol molecules could result in ~99% protection [22], this hypothesis has been confirmed in this study.

The use of natural products (especially of plant origin) as green inhibitors for mild steel in HCl solution has been reported in the literature. Gunasekaran and Chauhan [28] studied the inhibitive effect of zenthoxylum alatum plant extract on corrosion of mild steel in 15 wt.% HCl in the temperature range of 30-80°C. They found out that the inhibition efficiency decreased with increasing temperature. Rajiv et al [7] studied the corrosion inhibition of mild steel in 1 M HCl in the presence of 300 mg/L raw, ripe and over ripe banana peel extract. They found that the inhibition efficiencies of raw, ripe and over banana peel were 89, 82 and 77% in the presence of 300 mg/l of the extracts at 26°C. Jose et al [3] found out that the inhibition efficiencies of mango, orange, passion fruit and cashew fruit peels were 96, 95, 96 and 93 % for carbon steel immersed in 1 M HCl solution conatining 400 mg/L of the extracts for 24 h at 25°C. Ostovari et al. [16] reported the inhibition efficiency of 37.95% for mild steel in 1 M HCl containing 1.2 g/l of henna extract at 60°C for 6 h. Gunasekaran [15] reported the inhibition efficiency of 94% for mild steel immersed in 1 M HCl containing 400 ppm for justicia gendarussa extract at 60°C for 1 h. Okafor el al.[8] investigated the corrosion inhibition of mild steel by phyllanthus amarus extract. They found out that the leaves, seeds and combination of leaves and seeds gave inhibition efficiencies of 74.9%, 66.1% and 48.8 % for mild steel in 5 M HCl solution containing 4 g/l of the extracts at 40°C for 1 h. The inhibition effect of bamboo leaf for cold rolled steel was investigated by Xianghong et al [31]. They reported the inhibition efficiency of 55.6% for cold rolled steel in 5 M HCl in the presence of 200 mg/L of bamboo extract at 20°C. In comparison to this work, the corrosion inhibition performance of durum wheat is relatively good because most of the corrosion inhibition studies by plant extracts were done at low concentration of HCl solution. The inhibition efficiency of 77.64 ± 0.29 % was obtained at 60°C for 24 h immersion time. The results show that DW is still effective in the aggressive conditions investigated.

Some factors have been considered to evaluate the commercial viability of the green inhibitors: the cost analysis of the various optimum concentration of propargyl alcohol, 2- mercapto benzimidazole and durum added to 1L of 15 wt.% HCl solution is presented in Table 6. As can be seen from the table, the cost of the green corrosion inhibitor (durum wheat) is the cheapest compared to the commercial corrosion inhibitors. This is an advantage since price is one of the key factors to be considered in the development of corrosion inhibitors, especially if it is going to be used on a large scale. Also, the simplicity of the production process of durum wheat is another positive point since it does not require the addition of different chemicals or chemical synthesis, unlike the commercial inhibitors.

Table 6. Cost analysis of the optimum concentration of the studied inhibitors in 15 wt.% HCl solution.

Inhibitor	Quantity purchased	Cost (£)	Cost of optimum inhibitor in 1L HCl solution
Propargyl alcohol	100 ml	20.60	£1.44
2-mercaptobenzimidazole	100 g	15.50	£1.09
Durum wheat	5 000 g	5.50	£0.77

The inhibitive effect of durum wheat on the corrosion of mild steel may be due to the presence of adsorption sites (– C=O, -CN, -NH and pi electrons) in durum wheat molecules that donate their unshared lone pair electrons (non-bonding electrons) to the vacant 3d-orbitals of iron atoms. These functional groups can be seen in from Fig. 1.

Further work will be carried out to understand the chemical composition of the adsorbed film by X-ray photoelectron spectroscopy (XPS). Electrochemical impedance spectroscopy (EIS) will be also be investigated.

Conclusion
1. The hypothesis that durum wheat could be a promising corrosion inhibitor for mild steel in acidic solution has been confirmed.
2. Durum wheat can act as green corrosion inhibitor for mild steel in 15 wt.% HCl over the range of temperature (20-60ºC) and immersion time (5-24 h) with efficiencies varying from 97% (5 hours at room temperature) down to 77% (24 hrs, 60ºC)
3. The optimal concentration for durum wheat was similar for the commercial corrosion inhibitors (7 g/l) but durum wheat is cheaper,
4. The adsorption of the inhibitors followed Langmuir adsorption isotherm model, and FTIR confirmed the expected bonds to be present.
5. The corrosion inhibition performance of durum wheat and 2-mercaptobenzimidazole is influenced by variation of time and temperature.
6. SEM-EDS show modified surfaces of mild steel in the presence of the studied inhibitors.
7. Further work is needed to fully understand the adsorption mechanism at metal-solution interface.

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