Corrosion inhibition of mild steel by an effective imidazoline derivative based on waste oil in hydrochloric acid

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ABSTRACT

An efficient imidazoline derivative (WOI) based on waste oil was synthesized and its inhibition effect on mild steel corrosion in 1.0 M HCl solution was investigated using gravimetric measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy and energy dispersive spectrum. Results revealed that WOI showed good inhibition performance for mild steel in 1.0 M HCl. Potentiodynamic polarization study indicated that the WOI inhibitor acted as mixed-type inhibitor, and predominantly cathodic. EIS measurements suggested that the inhibition efficiency increased with increasing WOI inhibitor concentration and the maximum value of inhibition efficiency was 93.6% at 200 mg/L. Adsorption of WOI inhibitor on mild steel surface in 1.0 M HCl is spontaneous and obeys Langmuir adsorption isotherm. Both the physical and chemical adsorption existed for the WOI inhibitor adsorption on mild steel surface, and the physical adsorption is predominant. Meanwhile, the activation energy E_a and some thermodynamic parameters (ΔH^*, ΔS^*) were calculated to give insight into the inhibition mechanism.

Keywords: Mild steel; Inhibition; Waste oil; Polarization; EIS

1. Introduction

Mild steel is a popular metal material which has been commonly used as structural materials in petroleum and chemical engineering [1–6]. However, mild steel can be easily corroded at different environments, especially when exposed to HCl solution. The corrosion of mild steel will cause significant damage to economy and even human safety. Till now, numerous anticorrosion methods have been explored to protect mild steel from acid corrosion [7–9]. The utilization of organic inhibitors has been found to be one of the most economical and efficient ways [10–12]. The organic inhibitors work by adsorbing on to mild steel surface to form a protective film to restrain the aggressive acid attack. Their inhibition effectiveness does not only depend on the corrosive media, but also the chemical structure [13–15].

Generally, the most efficient inhibitors are those molecular structure contains nitrogen, sulfur, oxygen, heterocyclic/aromatic rings, multiple bonds or polar functional groups [16–18], which acts as adsorption centers on mild steel surface to form a physical barrier to hinder the corrosion reaction. The imidazole derivatives have been considerably applied for inhibition of metal corrosion due to its typical molecular structure. Wang [19] has studied the inhibition behavior of imidazole derivative for aluminum corrosion in acidic media and found that the inhibitor exhibited a high inhibition efficiency of 97.5%. Two other imidazole derivatives acted as anodic inhibitors for mild steel in 1.0 M hydrochloric acid and the maximum inhibition efficiency reaches 98.04% when the inhibitor concentration was 10^{-3} mol/L [20].

With increasing consideration of undesirable toxicity to the environment and human when employing these

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organic compounds, their widespread application has been limited. Therefore, it is an urgent and significant demand to look for "green" and "non-toxic" organic inhibitors. Much attention has paid to the natural products, such as vegetable oils [21,22], plant extracts [23–25], and derivatives based on them for their low cost and environmental friendless. Thymus vulgaris plant extract has been used as an eco-friendly corrosion inhibitor for stainless steel 304 in 1.0 M HCl solution [26]. The inhibition efficiency of Atlas cedar essential oil exceeded 88% at 1 g/L for steel in 1 M hydrochloric acid [27]. Waste oil is a kind of inferior oil and over 4 million tons of them was produced in china every year, which inevitably bring remarkable pollution to environment and cause a huge waste of resources.

Based on the consideration that organic compounds containing N, O, heterocyclic rings presents excellent inhibition efficiency for mild steel in acidic solution and to take advantage of waste oil, in the present work, an efficient imidazoline derivative based on waste oil was synthesized and theinhibition performance on mild steel in 1.0 M HCl solution was systematically investigated using

weight loss measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Meanwhile, the influence of temperature and immersion time on the inhibition effect was also discussed.

2. Experimental

2.1. Materials

The corrosive solution 1.0 M HCl was prepared from diluting 37 wt.% HCl (analytical grade, Sinopharm Chemical Reagent Co., Ltd.) with double distilled water. Waste oil (obtained from local market) was used to synthesize the imidazoline derivative according to the scheme presented in Fig. 1 and the main physicochemical properties of the obtained waste oil are shown in Table 1. Firstly, the obtained waste oil was filtered and then reacted with triethylenetetramine (Sinopharm Chemical Reagent Co., Ltd.) at 140–160°C under magnetic stirring for about 4.5 h. Then, the mixture was heated up to 200–210°C and refluxed to com-
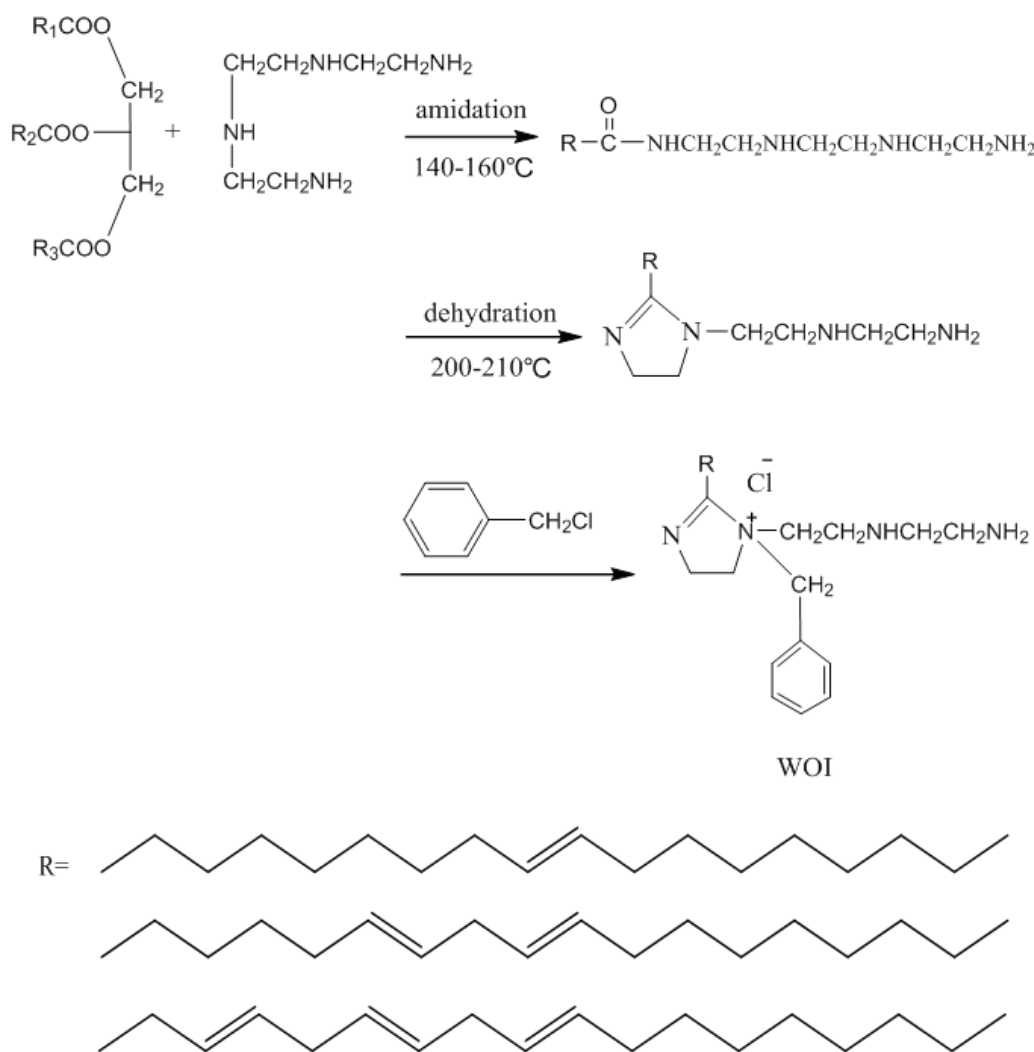

Fig. 1. Preparation scheme of studied imidazoline derivative (WOI).

Table 1
The main physicochemical properties of the obtained waste oil

Saponification value	223.15 mg KOH/g
Acid value	0.248 mg KOH/g
Water content	2.36%

plete the cyclizing of imidazoline. The dehydration process was monitored by thin layer chromatography (TLC) and the amount of produced water. Laterly, the obtained imidazoline derivative was reacted with benzyl chloride (Sinopharm Chemical Reagent Co., Ltd.) at about 110°C for about 3 h to enhance its water solubility. Finally, the raw product was purified through column chromatography using the mixture of trichloromethane and ethyl acetate.

FTIR (Nexus670, NICOLET) was performed in the wave-number range from 400 to 4000 cm^{-1} to analyze the structure of the purified product (designated as WOI), and the result was depicted in Fig. 2. Characteristic peaks located at 2924 cm^{-1} and 2853 cm^{-1} correspond to the asymmetric stretching and symmetric stretching vibration of C-H. The peak at 1745 cm^{-1} is ascribed to the C=O stretching vibration which disappeared in Fig. 2b. It is obvious that a strong peak at 1606 cm^{-1} can be observed for obtained WOI, which is correlated to the C=N bond in the imidazole ring. Additionally, another peak located at 699 cm^{-1} may be due to single substitution in benzene ring. Furthermore, the product was characterized using ^{1}H-NMR spectrophotometer (DMX-500, BRULCER.CO.) of 500 MHz. During the measurements, deuterated chloroform and TMS were used as the solvent and standard, respectively. Fig. 3 shows the ^{1}H-NMR spectra of obtained WOI inhibitor. It can be seen that the chemical shift located at 7.26 ppm corresponds to the H in the benzene ring. And peaks at 2.77 and 3.42 ppm were related to proton of NH and imidazole ring. The strong peak at 1.28 ppm was ascribed to that of CH$_2$. From the above analysis, it can be deduced that the target compound had been synthesized.

2.2. Weight loss experiments

The mild steel specimens of dimension 50 mm × 25 mm × 5 mm were used for weight loss experiments, which were taken out according to the previously described procedure [28,29]. The chemical composition of mild steel is shown in Table 2. The corrosion rate C_R (mg cm^{-2} h^{-1}), inhibition efficiency (IE%) and surface coverage (θ) were calculated using the following equations [30]:

$$C_R = \frac{87.6 \times W}{A \times t \times \rho} \tag{1}$$

$$IE(\%) = (1 - C_{Rinhi}/C_{Rfree}) \times 100 \tag{2}$$

$$\theta = 1 - C_{Rinhi}/C_{Rfree} \tag{3}$$

where W is the average mass loss (mg), A is the working area (cm^2), t is immersion time (h) and ρ is the density (7.86 g cm^{-3}). C_{Rinhi} and C_{Rfree} are the calculated corrosion rates for mild steel with and without inhibitors, respectively.
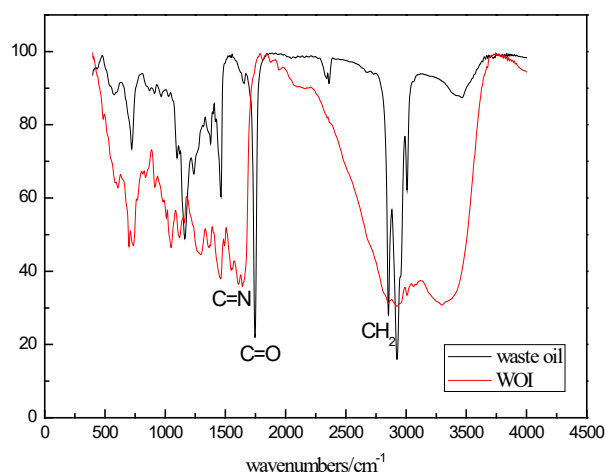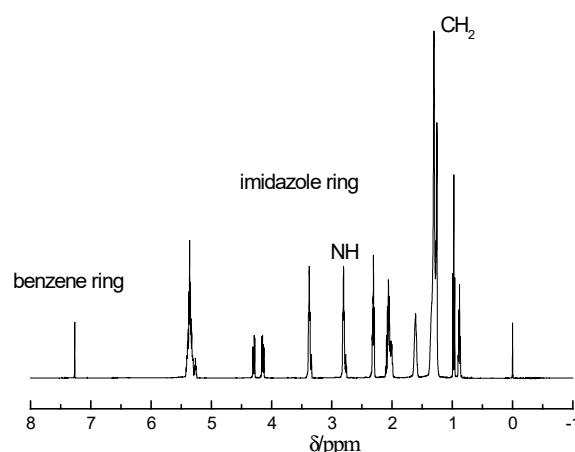

Fig. 2. FTIR of the (a) waste oil; (b) obtained WOI.

Fig. 3. ^{1}H-NMR of the obtained WOI.

Table 2
Chemical composition (mass fraction, wt. %) of Q235 mild steel samples

C	0.16
Mn	0.53
Si	0.30
S	<0.055
P	<0.045
Fe	Bal.

2.3. Electrochemical measurements

All the electrochemical measurements were performed with a traditional three electrode electrolytic cell consisting of cylindrical mild steel as working electrode, a large grid of platinum (2.0 cm^2) as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The working area of cylindrical mild steel is 0.50 cm^2. Prior to electrochemical measurements, the working area was abraded

successively with different grades of SiC emery papers, polished to mirror with 2.5 μm diamond paste, and rinsed with acetone. Then the polished working electrode was immersed into testing solution for 1 h when the open circuit potential (OCP) reached a steady state. The potentiodynamic polarization curves were recorded at a scan rate of 1 mV/s in the potential range of E_{ocp}–250 mV to E_{ocp}+250 mV. EIS measurements were conducted in the frequency range from 100 KHz to 10 mHz at E_{ocp} with 5 mV amplitude of AC perturbation using an impedance measurement unit (PARSTAT 2273).

2.4. Surface investigation

The surface morphologies of mild steel specimens after immersion in 1.0 M HCl without and with WOI inhibitor were recorded using SEM model Hitachi SU80 instrument. The surface composition of mild steel specimens at different conditions was also investigated by a EDX detector.

3. Results and discussion

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The weight loss results of mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of WOI inhibitor at 30°C are given in Table 3 and the relationship between inhibition efficiency and WOI inhibitor concentration is shown in Fig. 4. It is apparent that the corrosion rate reduces sharply from 4.35 mg cm^{-2} h^{-1} to 0.68 mg cm^{-2} h^{-1} with addition of 30 mg/L WOI inhibitor compared to the blank, which may be due to the formation of a protective film on mild steel to retard the aggressive acid attack [31]. Additionally, the corrosion rate decreases with increasing WOI inhibitor concentration, which is ascribed to the stronger adsorption of WOI molecules on mild steel surface at higher concentrations. Consequently, the inhibition efficiency increases with the increase of WOI inhibitor concentration from 30 mg/L to 200 mg/L, and the maximum value of inhibition efficiency is 96.6% at 200 mg/L. This finding suggests that WOI compound acts as an excellent corrosion inhibitor for mild steel in 1.0 M HCl solution. It is noticeable that the inhibition efficiency is over 80% when the concentration is low (30 mg/L), indicating that WOI compound exhibits good inhibition effect at low concentration.

Table 3
The weight loss parameters for mild steel in 1.0 M HCl containing different concentrations of WOI inhibitor at 30°C

c (mg/L)	C_R (mg cm^{-2} h^{-1})	η(%)	Θ
0	4.35±0.06	–	–
30	0.68±0.02	84.4	0.844
50	0.56±0.03	87.1	0.871
100	0.31±0.01	92.9	0.929
150	0.22±0.02	94.9	0.949
200	0.15±0.01	96.6	0.966

3.1.2. Adsorption isotherm

The adsorption behavior of inhibitor molecules on metal surface can be expressed through adsorption isotherm [32]. Therefore, to get more valuable information about the adsorption of WOI inhibitor on mild steel surface, various adsorption isotherms, including Frumkin, Langmuir and Temkin isotherms, are applied to fit the correlation of surface coverage (θ) and WOI inhibitor concentration (c). It can be seen that (Fig. 5) a linear relationship can be established between c/θ and c with the linear association coefficients over 0.99, and the slope is close to 1, indicating that the adsorption of WOI molecules on mild steel surface obeys the Langmuir adsorption isotherm [33–35]:

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + c \tag{4}$$

where θ is surface coverage obtained from weight loss measurements, K_{ads} is the equilibrium constant which can be derived from the intercept.
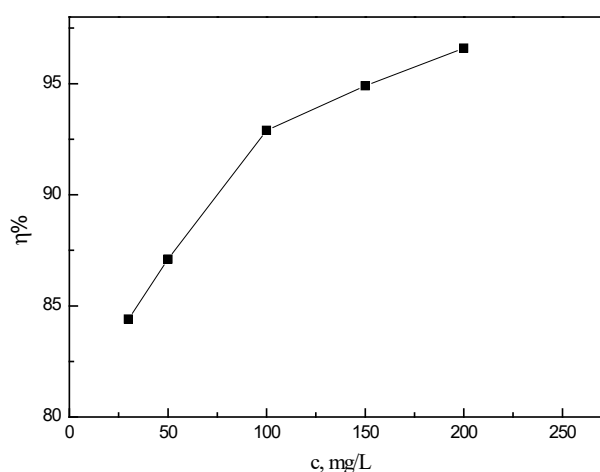

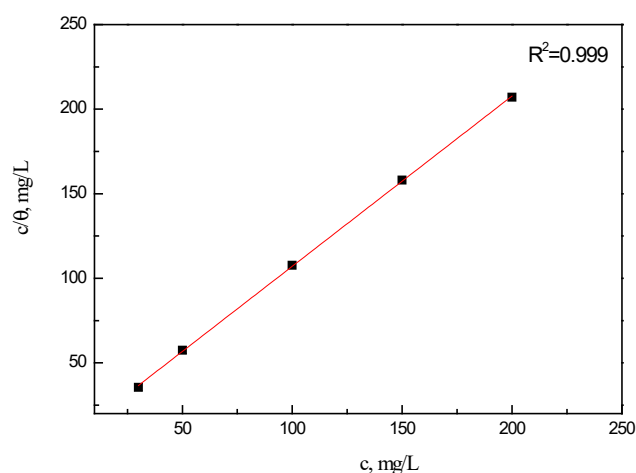Fig. 4. Relationship between inhibition efficiency and WOI inhibitor concentration.

Fig. 5. Langmuir adsorption isotherm for WOI inhibitor adsorption on to mild steel surface.

In addition, the standard free energy of adsorption ΔG_{ads}^0 can be obtained from the following relation [36,37]:

$$-\Delta G_{ads}^0 = -RTln\left(55.5K_{ads}\right) \tag{5}$$

where R represents the universal gas constant and T corresponds to the absolute temperature (K).

The value of ΔG_{ads}^0 for WOI inhibitor adsorption on mild steel was calculated to be –26.5 kJ/mol. The negative value of valuable indicates that the adsorption of WOI inhibitor molecules on mild steel surface is spontaneous [38]. Generally, a value of ΔG_{ads}^0 around –20 kJ/mol or lower suggests the physical adsorption mechanism by electrostatic interaction, whereas a value of ΔG_{ads}^0 around –40 kJ/mol or higher reveals the chemical adsorption mechanism involving charge sharing or transfer from the organic molecules to the metal surface to form a coordinate bond [39]. Therefore, it is rational to deduce that both the physical and chemical adsorption existed for the WOI inhibitor adsorption on mild steel surface, and the physical adsorption is predominant.

3.1.3. Effect of temperature

Weight loss measurements were conducted at different temperatures ranging from 30°C to 60°C in the absence and presence of 200 mg/L WOI inhibitor and the results are listed in Table 4. Obviously, in the uninhibited solution, the value of C_R increased from 4.35 to 28.5 mg cm^{-2} h^{-1} with rising temperature from 30°C to 60°C, suggesting that the dissolution rate of mild steel in 1.0 M HCl solution gets faster at higher temperatures. With addition of 200 mg/L WOI inhibitor, the value of C_R increased from 0.15 to 4.19 mg cm^{-2} h^{-1} with the temperature rises from 30°C to 60°C. Additionally, the inhibition efficiency reduces from 96.6% to 85.3% with the increase of temperature from 30°C to 60°C, which may be related to the larger desorption rate of WOI inhibitor molecules on mild steel surface at higher temperatures [40]. According to the previous study, the decrease of inhibition efficiency with increasing temperature suggests physical adsorption of organic molecules onto mild steel surface [41,42]. Thus, in our case, the adsorption of WOI inhibitor on mild steel surface mainly follows physical adsorption, which result agrees well with that deduced from the standard free energy of adsorption. It is clear that a linear relationship between $log(C_R)$ and $1000/T$ can be established as depicted in Fig. 6. The apparent activation energy (E_a) for mild steel dissolution in 1.0 M HCl solution in the absence and presence of 200 mg/L WOI inhibitor can be calculated

according to the Arrhenius equation [43–45] and the results are give in Table 5:

$$\log\left(C_R\right) = \frac{-E_a}{2.303RT} + \log\left(A\right) \tag{6}$$

where R is the universal gas constant, T is absolute temperature, A is the pre-exponential factor.

Moreover, various activation parameters, such as enthalpy of activation (ΔH_a^0) and entropy of activation (ΔS_a^0) for mild steel dissolved in 1.0 M HCl solution without and with 200 mg/L WOI inhibitor can also be calculated according to the transition state equation [46,47]:

$$C_R = RT / Nh\exp(-\Delta H_a^0 / RT)\exp(\Delta S_a^0 / R) \tag{7}$$

where C_R is the corrosion rate at different testing temperature, N is Avogadro's number and h is Plank's constant.

The apparent activation energy (E_a) can be calculated from the slope of the straight line shown in Fig. 6, and enthalpy of activation (ΔH_a^0) and entropy of activation (ΔS_a^0) can be obtained from the slope and intercept of the straight line shown in Fig. 7, respectively. From Table 5, it is clear that the value of E_a with 200 mg/L WOI inhibitor (93.9 KJ mol^{-1}) is higher than that without WOI inhibitor (44.1 KJ mol^{-1}). The increase of E_a value with addition of organic inhibitor compared to the blank can be ascribed to the electrostatic interaction between WOI inhibitor molecules and mild steel surface, indicating the physical adsorption mechanism of WOI inhibitor on mild steel surface [48]. This finding is in good accordance with that inferred from that of the adsorption isotherm. The above conclusions have also been reported by other researches [49–51]. Meanwhile, the positive value of ΔH_a^0 for both the uninhibited and inhibited samples reveals the endothermic nature of mild steel dissolution in 1.0 M HCl solution. The larger value of ΔH_a^0 with addition of 200 mg/L WOI inhibitor (91.3 KJ mol^{-1}) compared to the blank (41.4 KJ mol^{-1}) suggests the dissolution rate of mild steel gets slower in the presence of 200 mg/L WOI inhibitor. Moreover, the larger negative value of ΔS_a^0 in the presence of 200 mg/L WOI inhibitor is due to formation of ordered stable film of WOI molecules on mild steel surface [52].

3.1.4 Effect of immersion time

The influence of immersion time on the inhibition efficiency for mild steel in 1.0 M HCl solution with addition of 200 mg/L WOI inhibitor is shown in Fig. 8. It is obvious that the inhibition efficiency initially increases from 96.6%

Table 4
The weight loss parameters for mild steel in 1.0 M HCl solution in the absence and presence of 200 mg/L WOI inhibitor at different temperatures

Temperature (°C)	Blank C_R (mg cm^{-2} h^{-1})	200 μM C_R (mg cm^{-2} h^{-1})	η(%)
30	4.35	0.15	96.6
40	8.45	0.77	90.9
50	20.3	2.43	88.0
60	28.5	4.19	85.3

Table 5
The activation parameters for mild steel dissolution in 1.0 M HCl solution without and with 200 mg/L WOI inhibitor

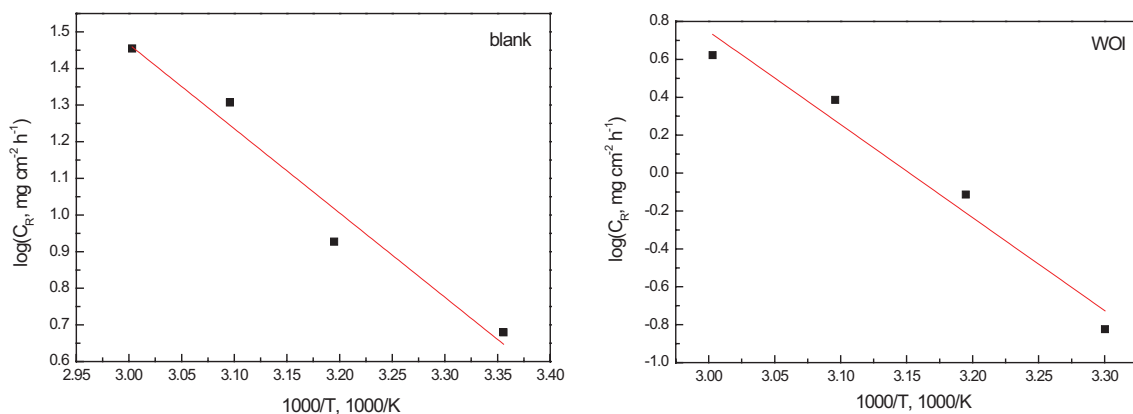| 1.0 M HCl			
C (mg/L)	E_a KJ mol^{-1}	ΔH_a^0 KJ mol^{-1}	ΔS_a^0 J mol^{-1} K^{-1}
0	44.1	41.4	93.5
200	93.9	91.3	−45.2

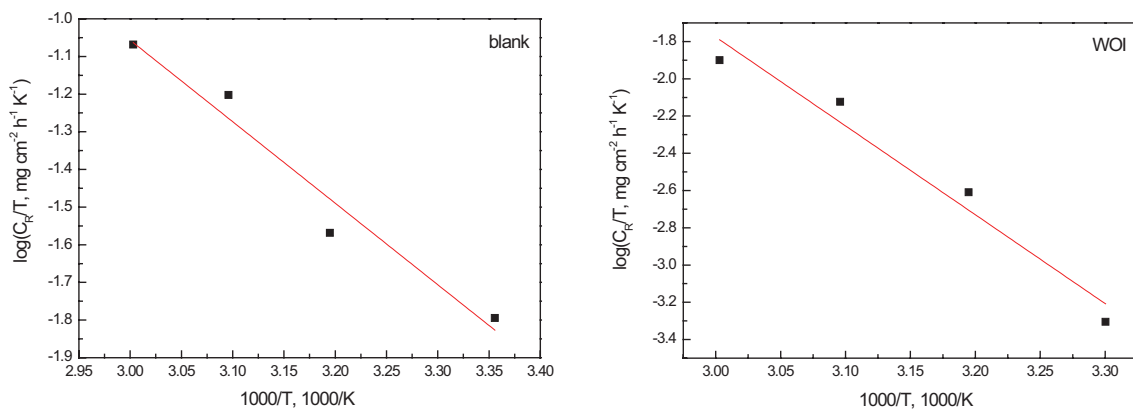Fig. 6. Arrhenius plot of log (C_R) vs. 1000/T in the absence and presence of 200 mg/L WOI inhibitor.

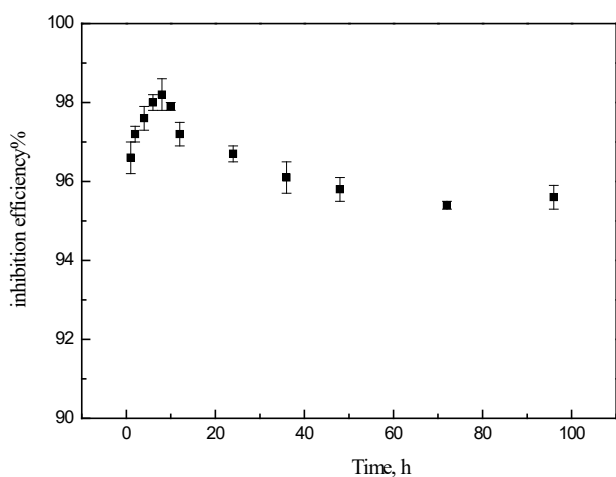Fig. 7. log (C_R/T) vs. 1000/T in the absence and presence of 200 mg/L WOI inhibitor.

Fig. 8. Dependence of inhibition efficiency on immersion time for mild steel in 1.0 M HCl solution in the presence of 200 mg/L WOI inhibitor.

to 98.2% with increasing immersion time from 2 h to 8 h, which may be due to the strong adsorption and more and more active sites was occupied by WOI inhibitor molecules. After 8 h immersion time, the inhibition efficiency slowly decreases with increasing immersion time. It is noticeable

that during our immersion time (96 h), the inhibition efficiency is still over 95%, suggesting the long-term inhibition effect of WOI inhibitor for mild steel in 1.0 M HCl solution.

The comparison of inhibition effect between inhibitors reported in literatures and the present work is shown in Table 6. It is clear that the inhibitor imidazole derivative P1 reported in literature 20 exhibited the highest inhibition efficiency of 98.0% at a concentration of 400 mg/L for mild steel in 1.0 M HCl solution. While some inhibitors showed smaller values of the inhibition efficiency, although with addition of larger concentration [1,28]. However, the effective imidazole derivative P1 may be hard to fabricate due to its complicated molecular structure and the synthesizing procedure was not reported yet [20]. It is noticeable that the effect of immersion time on the inhibition efficiency was not investigated for most of the studies. Therefore, based on the experimental results, it is rational that the waste oil based imidazline derivative has the practical potential for protection of mild steel in 1.0 M HCl solution due to its good inhibition effect and long-term inhibition performance.

3.2. Electrochemical measurements

3.2.1. Open circuit potential curves

The open circuit potential for mild steel in 1.0 M HCl solution without and with different concentrations of WOI

Table 6
Inhibition effect of different inhibitors for mild steel in 1.0 M HCl solution reported in the literatures

Inhibitors	Maximum IE%	c (g/L)	Long-term effect	Ref.
Unsymmetrical Schiff's Base	92	0.6	no reported	[1]
2-aminobenzene-1,3-dicarbonitriles derivatives	97.8	0.1	no reported	[10]
Imidazole derivative P1	98.0	0.40	no reported	[20]
Imidazole derivative P2	96.5	0.46	no reported	[20]
cefalexin drug	92.1	0.5	no reported	[28]
1-(4-methyl-phenyl)-1H-pyrrole-2,5-dione	97.5	0.187	no reported	[30]
3,5-bis(4-methoxyphenyl)-4-amino-1,2,4-triazole	98	0.1	no reported	[37]
Waste oil based imidazoline	96.6	0.20	>95% at 96 h	This work

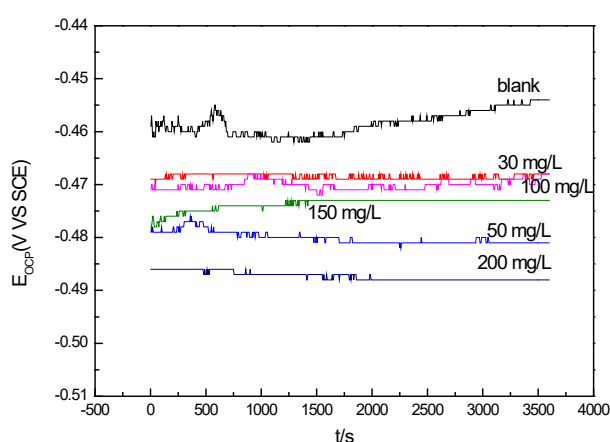Fig. 9. Open circuit potential for mild steel in 1.0 M HCl solution without and with different concentrations of WOI inhibitor.
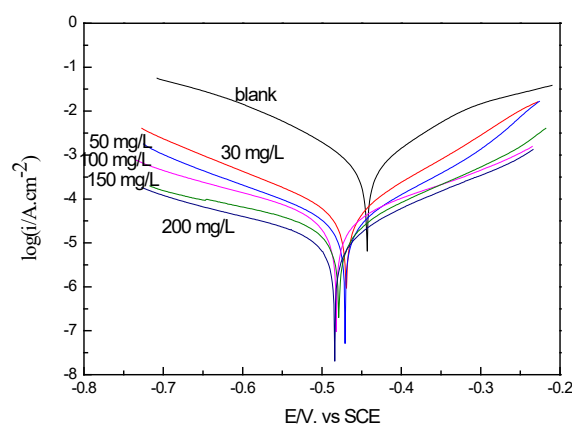

Fig. 10. Potentiodynamic polarization curves for mild steel in 1.0 M HCl solution without and with different concentrations of WOI inhibitor.

inhibitor is depicted in Fig. 9. In our experimental condition, the OCP reached a steady state after 1 h immersion time. It can be seen that the OCP moved in the negative direction with addition of different concentration of WOI inhibitor compared to the blank. This shift may be corresponds to the formation of adsorption film on mild steel surface.

3.2.2. Potentiodynamic polarization curves

Potentiodynamic polarization curves for mild steel in the absence and presence of different concentrations of WOI inhibitor in 1.0 M HCl solution at 30°C are shown in Fig. 10. It is clear from Fig. 10 that both the cathodic and anodic current densities decrease with addition of WOI inhibitor in to the corrosive media compared to the uninhibited, which may be due to the surface coverage of WOI molecules on mild steel surface [53]. In addition, the E_{corr} moves to the negative direction in the presence of different concentration of WOI inhibitor. Moreover, it can be seen that the shape of potentiodynamic polarization curves without and with WOI inhibitor are almost the same, revealing that WOI inhibitor inhibited the mild steel corrosion in 1.0 M HCl solution through adsorption on its surface and did not modify the dissolution mechanism [54]. Various electrochemical parameters, including corrosion potential (E_{corr}), corrosion current density (j_{corr}), cathodic Tafel slope(β_c) and

anodic Tafel slope (β_a) were calculated by Tafel extrapolation method and the values are listed in Table 7.

The inhibition efficiency η_p(%) obtained from potentiodynamic polarization measurements can be calculated as follows [55], and the results are also listed in Table 7.

$$\eta_P\% = (1 - j_{inhi} / j_{free}) \times 100\% \qquad (8)$$

where j_{inhi} and j_{free} are the corrosion current densities for the inhibited and uninhibited samples, respectively.

Table 7
Polarization parameters for mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of WOI inhibitor

C (mg/L)	E_{corr} (mV)	β_a (mV dec^{-1})	$-\beta_c$ (mV dec^{-1})	i_{corr} (μA cm^{-2})	η_P(%)
0	−442	94.6	107.8	496	−
30	−463	102.8	112.3	87.8	82.3
50	−465	105.7	115.7	73.4	85.2
100	−472	112.3	121.2	56.5	88.6
150	−476	108.1	125.6	42.1	91.5
200	−483	106.5	118.9	35.2	92.9

It is apparent from Table 7 that the value of I_{corr} decreases from 496 µA cm^{-2} to 42.1 µA cm^{-2} when the WOI inhibitor concentration increases from 0 to 200 mg/L, suggesting that WOI molecules strongly adsorb on the mild steel surface and exhibits excellent inhibition effect for mild steel in 1.0 M HCl solution. Meanwhile, the maximum displacement in E_{corr} is 41 mV when WOI inhibition concentration is 200 mg/L. It is reported that when the shift in E_{corr} is less than 85 mV, we can assume that the inhibitor is a mixed-type [56]. Therefore, WOI compound acts as a mixed-type inhibitor for mild steel in 1.0 M HCl solution, and predominantly cathodic. Additionally, the value of both β_c and β_a nearly remained constant, which further proves that the inhibition effect of WOI originates from the adsorption of WOI molecules on mild steel surface and blocking the available reaction sites [57].

3.2.3. EIS measurements

Fig. 11 represents the typical Nyquist diagrams of mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of WOI inhibitor. It can be seen that the Nyquist diagrams is remarkably influenced and the diameter of semicircles significantly increase with addition of WOI inhibitor compared to the blank. This observation indicates that the dissolution rate of mild steel in 1.0 M HCl solution is considerably suppressed by WOI inhibitor, which may be attributed to the adsorption of WOI molecules on mild steel surface [58,59]. With the increase of WOI inhibitor concentration, the diameter of the capacitive circle increases as well, suggesting that more and more WOI inhibitor molecules adsorb on to mild steel surface and forms a protective barrier to hinder the acid attack [60]. As deduced through both the EIS diagram features and the method proposed by Wit [61,62], the impedance spectra is composed of single depressed capacitive semi-circle in the blank solution while two in the presence of WOI inhibitor, correspond to the charge transfer process and adsorbed film capacitance, respectively. In addition, the unideal semicircle is attributed to the surface roughness and chemical inhomogeneity known as "dispersion effect" at the solid/liquid interface [63]. Therefore, the ideal capacitance c should be replaced by the constant phase element (CPE), which impedance can be represented using the following equation [64,65]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \tag{9}$$

where ω is the angular frequency, and n is a CPE exponent which represents the surface roughness.

Consequently, the electrochemical equivalent circuit shown in Fig. 12 is used to fit the EIS data. R_s is solution resistance, CPE_{dl} and R_{ct} represent double layer capacitance and charge transfer resistance, respectively. CPE_f and R_f correspond to the film capacitance and film resistance, respectively. The fitted results are listed in Table 8. The inhibition efficiency can be calculated by the following equation [66], whose values are also shown in Table 8.
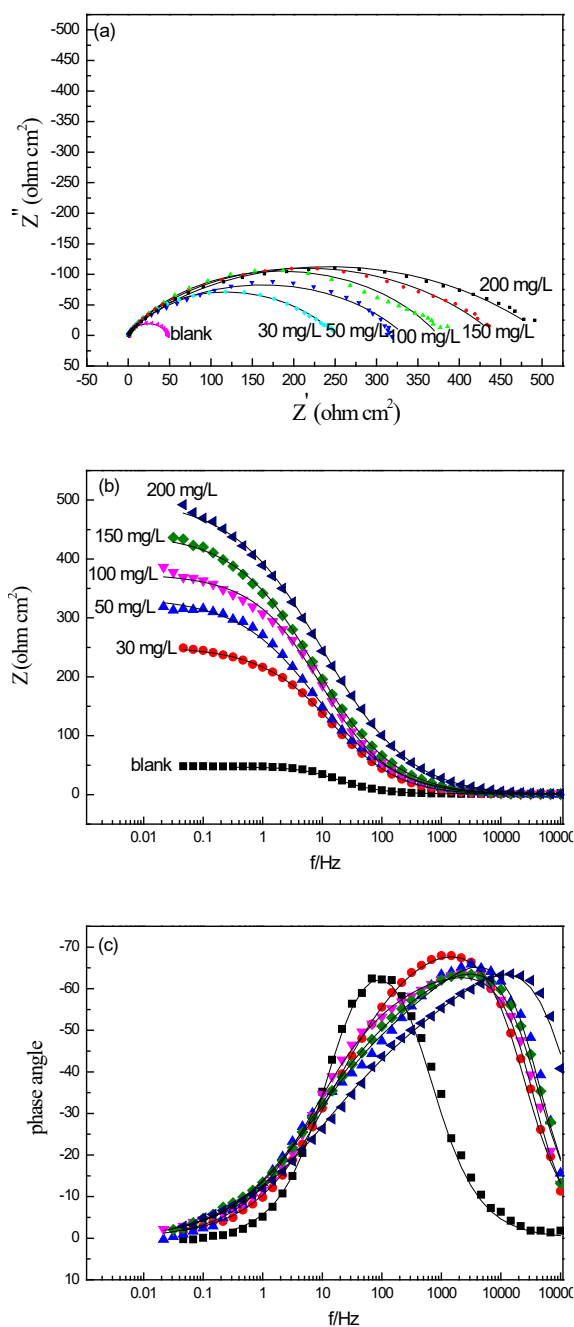

Fig. 11. Nyquist (a) and Bode (b) (c) diagrams of mild steel in 1.0 M HCl solution containing different concentrations of SOI inhibitor.

$$IE(\%) = (1 - R_p^{free} / R_p^{inhi}) \times 100 \tag{10}$$

where R_p^{free} and R_p^{inhi} are the total resistance in the absence and presence of different concentration of WOI inhibitor, respectively.

Inspection of Table 8 reveals that the value of R_{ct} increases significantly with addition of WOI inhibitor compared to the blank. Both R_f and R_{ct} increase with the increase of WOI inhibitor concentration, suggesting the lower dis-
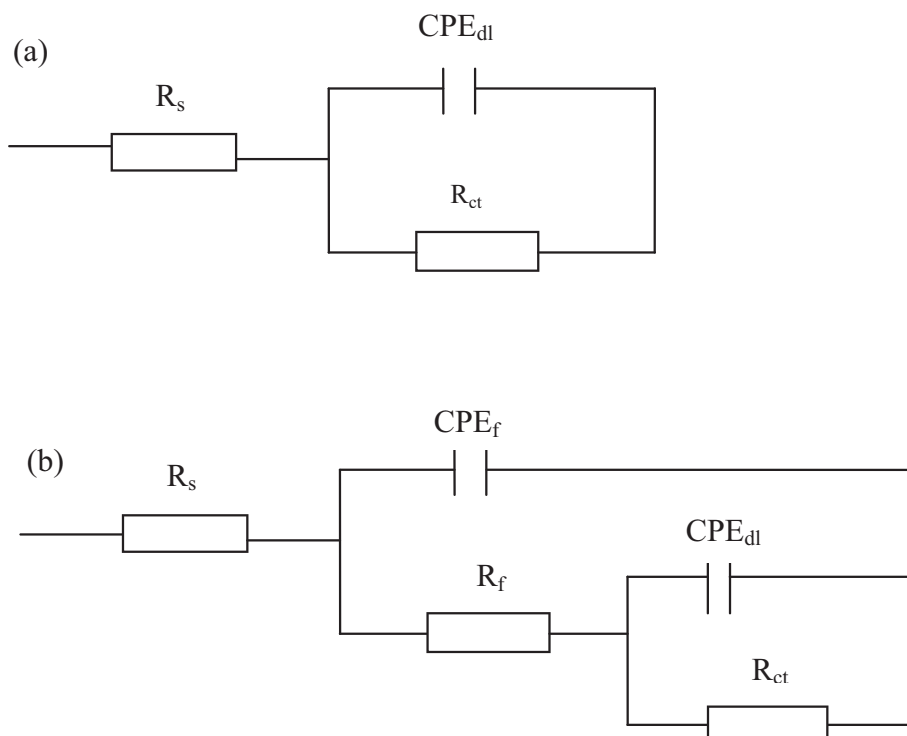
Fig. 12. Equivalent electrochemical circuit model used to fit the EIS data.

Table 8
EIS parameters for mild steel in 1.0 M HCl solution without and with different concentrations of WOI inhibitor

C (mg/L)	R_s (Ω cm^2)	R_f (Ω cm^2)	R_{ct} (Ω cm^2)	Q_{dl} (Ω^{-1}s^n cm^{-2})	$R_p = R_f + R_{ct}$ (Ω cm^2)	n_{dl}	η_{EIS} (%)
0	1.56	–	33.8	204	33.8	0.91	–
30	1.34	18.5	204.5	134	223	0.96	84.8
50	1.42	25.4	236.6	125	262	0.97	87.1
100	1.51	32.1	286.9	119	319	0.96	89.4
150	1.27	39.7	377.3	107	417	0.95	91.9
200	1.33	44.2	483.8	98	528	0.97	93.6

solution rate of mild steel in 1.0 M HCl solution in the presence of WOI inhibitor which is due to the adsorption of WOI molecules on mild steel surface. The highest value of R_{ct} is 483.8Ω cm^2 when the WOI inhibition concentration is 200 mg/L. However, the values of Q_{dl} show the reverse variation trend with R_{ct}, which decrease with the increase of WOI inhibitor concentration. This phenomenon can be explained by the increase substitution of WOI molecules for pre-adsorbed water on mild steel surface [67]. The value of n is related to the roughness of the surface. Generally, a larger surface roughness can be assumed with a smaller value of n [68]. It is seen that the values of n are over 0.9 for all the uninhibited and inhibited samples. And a little larger value of n can be observed with addition of WOI inhibitor than that of blank, revealing that the mild steel surface is smoother in the presence of WOI inhibitor and the surface roughness is improved due to the adsorbed protective film on mild steel surface.

3.3. Surface investigation

Fig. 13 shows the surface morphologies of mild steel in 1.0 M HCl solution in the absence and presence of 200 mg/L WOI inhibitor for 1 h. It can be seen that the mild steel surface is severely corroded in the absence of WOI inhibitor due to the aggressive acid attack (Fig. 13a). When 200 mg/L WOI inhibitor was added in to 1.0 M HCl solution, the mild steel surface is much smoother (Fig. 13b), suggesting that the synthesized WOI inhibitor could supply an effectively barrier to hinder the corrosion reaction on mild steel surface. EDX spectra were conducted to study the surface chemical composition of mild steel (Fig. 14). It is obvious that with addition of 200 mg/L WOI inhibitor, the characteristic peaks for nitrogen (N) and chlorine (Cl) can be observed, which further proved the presence of WOI molecules on mild steel surface.
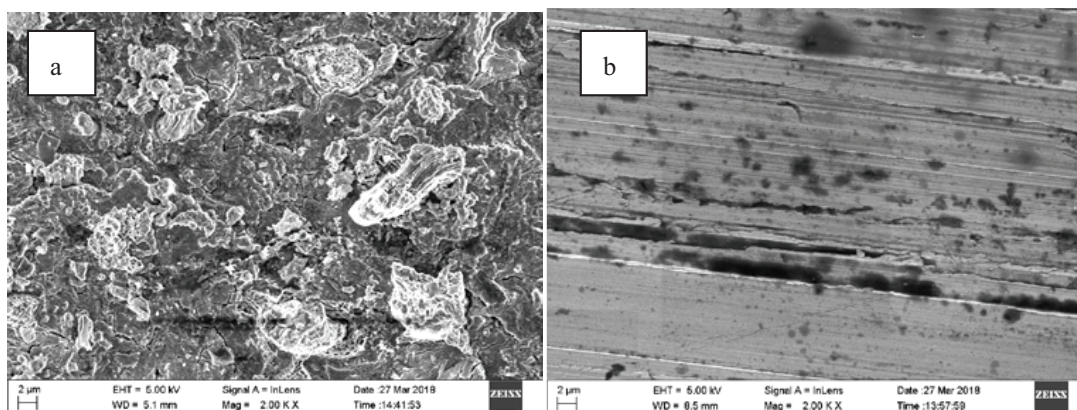
Fig. 13. SEM images of mild steel surface (a) in the absence and (b) in the presence of 200 mg/L WOI inhibitor (b) in 1.0 M HCl solution.
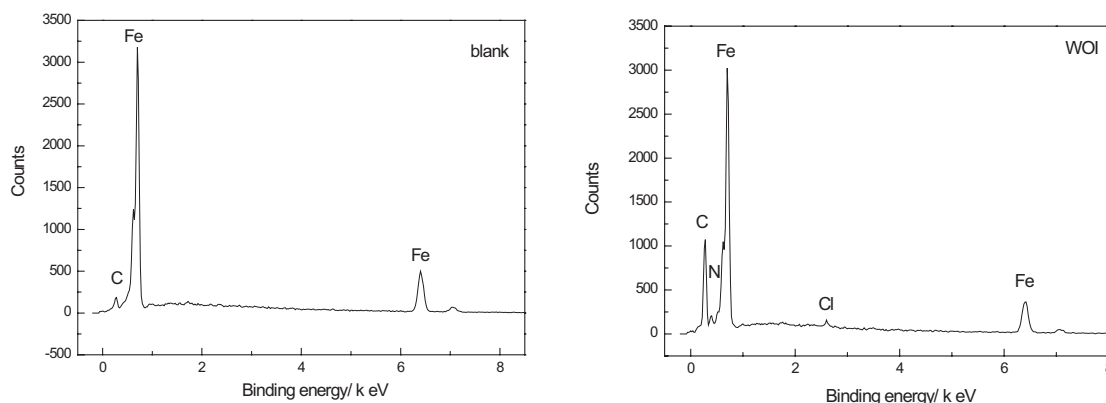

Fig. 14. EDX spectra of mild steel samples in1.0 M HCl solution without and with 200 mg/L WOI inhibitor.

4. Conclusions

An efficient imidazoline derivative (WOI) based on waste oil was synthesized and its molecular structure was characterized using FTIR. The inhibition behavior of WOI inhibitor for mild steel in 1.0 M HCl solution was investigated using gravimetric measurements, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscopy and energy dispersive spectroscopy. WOI proved to be a very good inhibitor for mild steel in 1.0 M HCl. The potentiodynamic study suggested that the WOI inhibitor acted as mixed-type inhibitor, and predominantly cathodic. EIS measurements suggested that the inhibit ion efficiency increased with increasing WOI inhibitor concentration and the maximum value of inhibition efficiency was 93.6% at 200 mg/L. Adsorption of WOI inhibitor on mild steel surface in 1.0 M HCl is spontaneous and conforms to Langmuir adsorption isotherm. Increased value of E_a with addition of WOI inhibitor revealed the physical adsorption mechanism of WOI inhibitor on mild steel surface. SEM and energy dispersive spectroscopy were performed to confirm the presence of WOI molecules on mild steel surface.

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