Ranitidine Drugs as Non-Toxic Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Medium

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Abstract

Expired ranitidine was tested as a corrosion inhibitor for mild steel in 1 M HCl using different techniques: weight loss, potentiodynamic polarization, open circuit potential and electrochemical impedance spectroscopy. The polarization resistance (R_p) value increased with increase in the concentration of the inhibitor. Results obtained revealed that ranitidine performed excellently as a corrosion inhibitor for mild steel in this medium at 303 K. The protection efficiency increased with increasing inhibitor concentration. The maximum protection efficiency of 90% has been obtained at 400 ppm. On the other hand, the efficiency decreases with increasing temperature. The adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm model. The activation and thermodynamic parameters of dissolution and adsorption were calculated and discussed. The negative value of ΔG_{ads} (-40 kJ mol^{-1}) indicates spontaneous chemical adsorption. Results obtained from polarization, EIS and weight loss measurements are in good agreement with each other.

Keywords: mild steel, acid corrosion, weight loss, drugs, polarization.

Introduction

Mild steel is widely used as the constructional material in most of the major industries, particularly in food, petroleum, power production, chemical and electrochemical industries, especially due to its excellent mechanical properties and low cost. The major problem of mild steel is its dissolution in acidic medium. Corrosion of iron and mild steel in acidic aqueous solutions is one of the major areas of concern in many industries where acids are widely used for applications such as acid pickling, acid cleaning, acid descaling, and oil well acidizing. Because of general aggressiveness of acid solution, materials of construction are getting corroded easily.

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Corrosion is a thermodynamically feasible process as it is associated with decrease in Gibb's free energy. Corrosion is an afflicting problem associated with every use of metals. The damage by corrosion results in high cost for maintenance and protection of materials used. Development of methods to control corrosion is a challenge to scientists working in this area. Amongst various methods developed for corrosion protection, the use of inhibitors is an attractive and most practical method for the protection of metals in contact with corrosion media. Inhibitors reduce the corrosion of metallic materials by controlling the metal dissolution and consumption.

Majority of the well known inhibitors for the corrosion of steel in acidic medium are organic compounds containing nitrogen, sulphur, oxygen atoms, or N-hetero cyclic compounds with polar groups. A large number of scientific studies have been devoted to the subject of corrosion inhibitors for mild steel in acidic media [1-12]. Most of the commercial inhibitors are toxic in nature; therefore, replacement by environmentally benign inhibitors is necessary. Few non-toxic compounds have been investigated as corrosion inhibitors by some researchers [13-16]. Modified plastic waste was used as cheap and safe corrosion inhibitors for metals and alloys in different aqueous media [17-20]. The use of pharmaceutical compounds offers interesting possibilities for corrosion inhibition due to the presence of hetero atoms like nitrogen, sulphur and oxygen in their structure, and they are of particular interest because of their safe use, high solubility in water and high molecular size. Some of the azosulpha and antimalarial drugs have been reported as good corrosion inhibitors [21-23]. Also, the use of piperazine derivative drug as a corrosion inhibitor has been reported [24].

In a previous work expired ranitidine was investigated as corrosion inhibitor for aluminum alloy in acidic medium [25].

In the present work, expired ranitidine has been investigated as corrosion inhibitor for mild steel in hydrochloric acid using weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques. The survey of literature reveals that ranitidine is a non-toxic pharmaceutical compound used as a histamine H_2-receptor antagonist. Ranitidine has the commercial name of N[2-[[[5-[(dime-thylamino)methyl]-2furanyl]methyl]thio]ethyl]-N'-methyl-2-nitro-1,1-ethenediami-ne, HCl. Ranitidine contains N-atoms, O-atoms, S-atoms and π-bond in its structure, regarded as important factors for good inhibitor performance.

Materials and methods
Experimental procedure
The test material used was mild steel sample with the following composition (wt%): 0.18 C, 0.6 Mn, 0.05 S, 0.04 P, 0.1 Si and balance Fe. Test materials were abraded with different emery papers up to 1000 grade, cleaned with acetone, washed with double distilled water and properly dried prior to exposure. Analar grade HCl and double distilled water were used to prepare all solutions. Ranitidine hydrochloride (molecular weight of 350.87) from (SEDICO)

pharmaceutical company was used for the study. Fig. 1 shows the molecular structure of 'Ranitidine hydrochloride'.
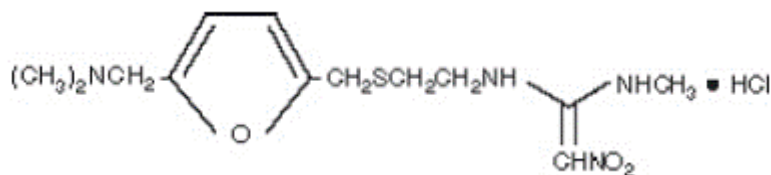

Figure 1. Molecular structure of ranitidine hydrochloride. {N[2-[[[5-[(dimethylamino) methyl]-2furanyl]methyl]thio]ethyl]-N'-methyl-2-nitro-1,1-ethenediamine, HCl}.

Weight loss measurements were performed on mild steel coupons having 2x2x0.2 inch size, in 1 M hydrochloric acid solution with different concentrations of the inhibitor. Weight loss of the metal coupons was noted after an immersing period of 7 days at the temperature range from 303 K to 333 K.
The potential of carbon steel electrodes was measured against the saturated calomel electrode (SCE) in 1 M HCl solution in the absence and presence of various inhibitor concentrations until the open circuit potential is reached. Potentiodynamic polarization studies were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostat and controlled by Tacussel corrosion analysis software model (Voltamaster 4) at a scan rate of 5 mVs^{-1} under static condition. A platinum electrode and a saturated calomel electrode (SCE) were used as auxiliary and reference electrodes, respectively. The working electrode was prepared from a cylindrical mild steel rod insulated with polytetrafluroethylene tape (PTFE). The area exposed to the aggressive solution was 1 cm^2. All the experiments were carried out at constant temperature of 30±1 °C.
AC impedance measurements were performed using Tacussel-Radiometer PGZ 301 Frequency Response Analyzer in a frequency range from 10^5 to 10^{-2} Hz with 10 points per decade. An AC sinusoid ±10 mV was applied at the corrosion potential (E_{corr}). The experiments were measured after 6 h of immersion.

Results and discussion
Weight loss measurements
Effect of inhibitor concentration
The weight loss results of mild steel in 1 M HCl in the absence and presence of various concentrations of the inhibitor are summarized in Table 1. The I.E (%) was calculated using the following equation:

$$I.E.(\%) = \frac{W2 - W1}{W2} \times 100 \qquad (1)$$

where W1 and W2 are weight loss of mild steel in the presence and absence of the inhibitor, respectively. The inhibition efficiency increased with increase in the concentration of the inhibitor.

Table 1. Degree of surface coverage (θ) and percentage inhibition efficiency (%IE) of the used inhibitor in 1 M HCl at 303 K, obtained from weight loss measurements.

conc.ppm	Wt. loss mg.cm^{-2}	Corrosion rate mg.cm^{-2} day^{-1}	θ	%IE
BLANK	48.6	9	0	0
50	18.3	3.2	0.609	60.9
100	17.5	2.9	0.649	64.9
150	16.2	1.7	0.75	75
250	15.4	1.5	0.81	81
400	14.3	0.98	0.89	89

Effect of temperature

To elucidate the mechanism of inhibition and to determine the kinetic parameters of the corrosion process, weight loss measurements were performed at 303, 313, 323 and 333 K. The effect of temperature on the corrosion inhibition efficiency of mild steel in the presence of the inhibitor is graphically represented in Fig. 2.
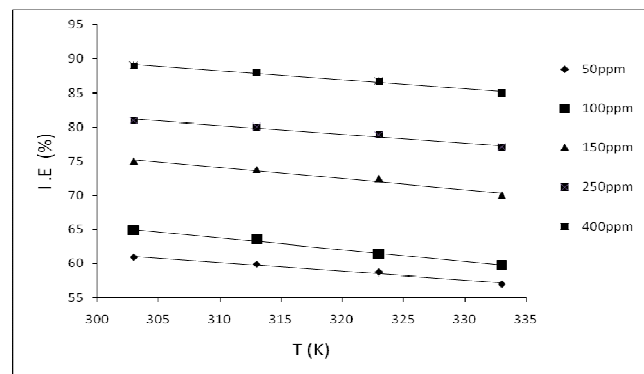
Figure 2. Effect of temperature on I.E for mild steel in 1 M HCl in the presence of different concentrations of the inhibitor.

The inhibition efficiency decreased with increase in temperature, leading to the conclusion that the protective film of these compounds formed on the mild steel surface is less stable at higher temperatures, which may be due to the desorption of some adsorbed molecules from the surface of the mild steel, due to which greater area of the metal is exposed to the acidic environment.

The apparent activation energy (E_a) of metal corrosion in acid media can be calculated from Arrhenius equation [26].

$$\ln(CR) = \frac{Ea}{RT} + A \tag{2}$$

where E_a is the apparent activation energy for the corrosion of mild steel, R is the universal gas constant, A is Arrhenius pre exponential factor and T is the absolute temperature. Fig. 3 depicts the plot of log CR vs. 1/T and the values of E_a obtained from the slope of the plot are given in Table 2.

The higher value of activation energy (E_a) in the presence of the inhibitor than in its absence is attributed to its physical adsorption; its chemisorption is pronounced in the opposite case [21, 27].
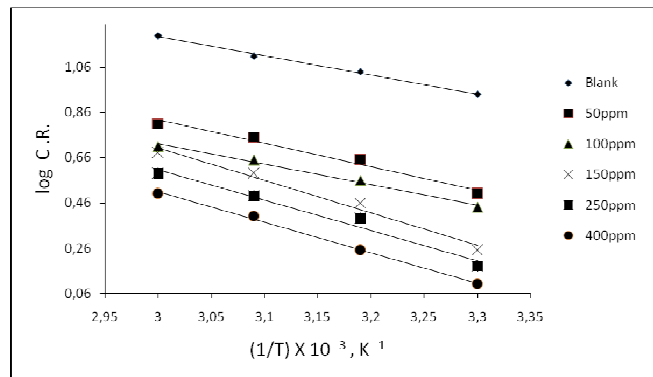

Figure 3. Arrhenius plot for mild steel in 1 M HCl solution in the absence and presence of different concentrations of the inhibitor.

Table 2 . Values of activation parameters for mild steel in 1 M HCl in the absence and presence of different concentrations of the inhibitor.

Inhibitor concentration (ppm)	E_a (kJmol^{-1})	ΔH_a (kJmol^{-1})	ΔS_a (JK^{-1}mol^{-1})
blank	40.37	37.48	-140.3
50	44.99	42.09	-132.54
100	47.96	45.12	-130.9
150	48.99	48.95	-125.73
250	51.32	52.35	-123.24
400	54.62	54.86	-119.87

In the present study the higher value of E_a for mild steel in presence of expired ranitidine compared to that in its absence is attributed to its physical adsorption. Szauer and Brand [28] explained that the increase in E_a can be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to acid environment.
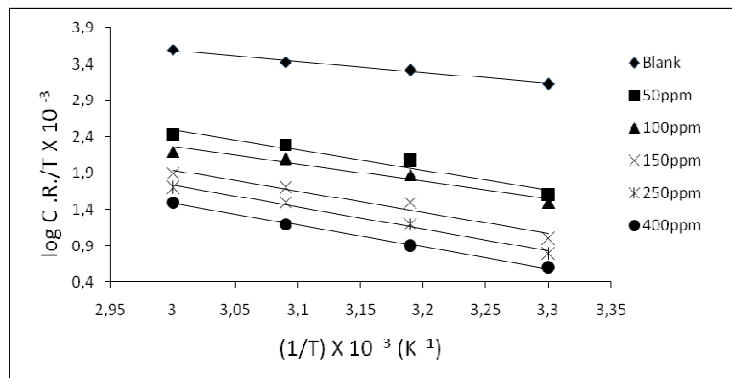

Figure 4. Transition state plot for mild steel in 1 M HCl solution in the absence and presence of different concentrations of the inhibitor.

An alternative form of Arrhenius equation is the transition state equation [26].

$$CR = \frac{RT}{Nh} e^{\frac{\Delta S_a}{R}} e^{\frac{\Delta H_a}{RT}}$$ (3)

where h is the Plank's constant, N is the Avogadro's number, ΔS_a is the entropy of activation, and ΔH_a is the enthalpy of activation. A plot of log (CR/T) vs. 1/T gave a straight line, as shown in Fig. 4 with a slope of (-ΔH /2.303R) and an intercept of [log(R/Nh) + (ΔS /R)], from which the values of ΔH_a and ΔS_a were calculated and listed in Table 2.

The positive values of ΔH_a for corrosion of mild steel in the presence and absence of the inhibitor reflect the endothermic nature of the metal dissolution process. The increase in ΔH_a with increase in the concentration of the inhibitor for mild steel corrosion reveals that decrease in mild steel corrosion rate is mainly controlled by kinetic parameters of activation [28].

The entropy of activation values are less negative for inhibited solutions than that for the uninhibited solutions. This suggests that an increase in randomness occurred while moving from reactants to the activated complex [29].
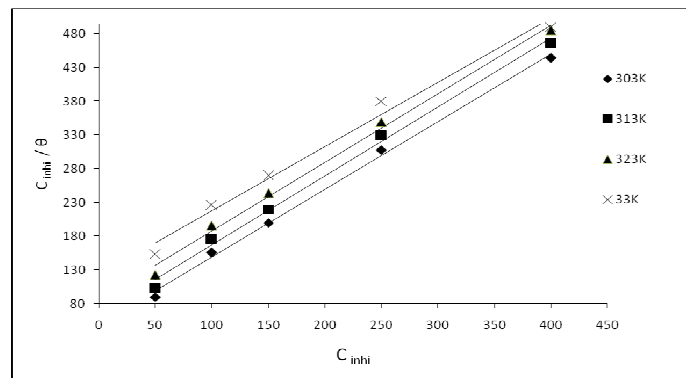

Figure 5. Langmuir adsorption isotherm for mild steel in 1 M HCl solution at various temperatures.

Adsorption isotherm and thermodynamic parameters
In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the organic adsorbate on the metal surface has to be known. The degree of surface coverage (Θ) for different concentrations of the inhibitor (C_{inhi}) has been evaluated. The data were tested graphically by fitting to various isotherms. A straight line with correlation coefficient nearly equal to 1.0 was obtained on plotting C_{inhi}/Θ against C_{inhi}, as shown in Fig. 5, suggesting adsorption of the compound on the mild steel surface following Langmuir adsorption isotherm model. It is interpreted from the graph that, adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm at all studied temperatures.

According to this isotherm, the surface coverage (Θ) is related [30] to inhibitor concentration C_{inhi} by equation (4)

$$\frac{C_{inhi}}{\theta} = \frac{1}{K_{ads}} + C \tag{4}$$

where K_{ads} is the equilibrium constant of the equilibrium adsorption process. This isotherm assumes that adsorbed molecule occupies only one site and it does not interact with other adsorbed species.

The K_{ads} values can be calculated from the intercept lines on the C_{inhi}/Θ axis. This is related to the standard free energy of adsorption (ΔG_{ads}) by equation (5):

$$\Delta G_{ads} = -RT \ln(55.5\ K_{ads}) \tag{5}$$

where R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/L. The values of ΔG_a for the inhibitor on the surface of mild steel are given in Table 3.

Table 3. Values of thermodynamic parameters for the adsorption of the inhibitor in 1 M HCl on mild steel at different temperatures.

T (K)	K (mol^{-1})	ΔG_{ads} (kJmol^{-1})	ΔH_{ads} (kJmol^{-1})	ΔS_{ads} (JK^{-1}mol^{-1})
303	55463	- 36.93	- 9.91	89.17
313	47092	- 37.73	- 9.91	88.88
323	42991	- 38.70	- 9.91	89.12
333	38294	- 39.58	- 9.91	89.10

The negative value of ΔG_a indicated spontaneous adsorption of the inhibitor on the mild steel surface. Generally, the magnitude of ΔG around -20 kJ/mol or less negative indicates electrostatic interactions between the inhibitor and the charged metal surface (i.e., physisorption). Those around -40 kJ/mol or more negative are indicative of charge sharing or transferring from organic species to the metal surface to form a coordinate type of metal bond (i.e., chemisorptions). In the present work, the calculated value ΔG at 303 K for mild steel is -37 kJ/mol, which indicates that adsorption of the inhibitor on the mild steel surface involves both physical and chemical process [31-34]. But the inhibition efficiency decreased with increasing temperature, indicating that the inhibitor adsorbed predominantly physically on the surface of mild steel. The enthalpy of adsorption (ΔH_{ads}) can be calculated from the rearranged Gibbs-Helmholtz equation:

$$\frac{\Delta G_{ads}}{T} = \frac{\Delta H_{ads}}{T} + K \tag{6}$$

The variation of $\Delta G_{ads}/T$ with $1/T$ gave a straight line with a slope of ΔH_{ads}, as shown in Fig. 6. The entropy of adsorption ΔS_{ads} was calculated using the following thermodynamic equation:

$$\Delta S_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T} \tag{7}$$

The calculated values of heat of adsorption and entropy of adsorption are listed in Table 3.
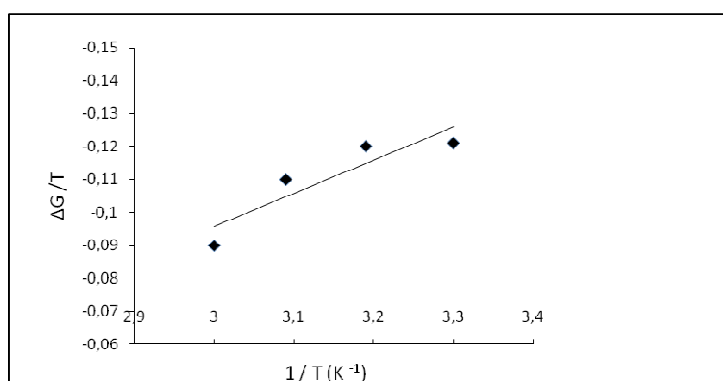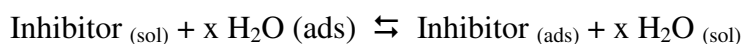

Figure 6. ΔG_{ads} /T versus 1/T plot for mild steel in 1 M HCl solution.

It is well known that adsorption is an exothermic phenomenon accompanied by a decrease in entropy [35]. In aqueous solutions the adsorption of the organic molecule is generally accompanied by desorption of water molecules [42].

$$\text{Inhibitor }_{(sol)} + x \; H_2O \text{ (ads)} \; \leftrightarrows \; \text{Inhibitor }_{(ads)} + x \; H_2O \;_{(sol)}$$

The negative sign of ΔH_{ads} indicated the exothermic process of adsorption of the inhibitor on mild steel surface in HCl. The positive value of ΔS_{ads} in the presence of the inhibitor can be attributed to the increase in the solvent entropy and more positive desorption entropy. It is also interpreted that the increase of disorderness is due to more water molecules which can be desorbed from the metal surface by one inhibitor molecule. Therefore it is revealed that decrease in the enthalpy is the driving force for the adsorption of the inhibitor on the surface of mild steel [36-39].

Mechanism of corrosion inhibition
In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface.

$$\text{Fe} + \text{Cl}^- \; \rightarrow \; (\text{FeCl}^-)_{ads}$$
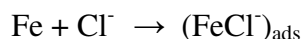
In acidic solution, the oxygen, sulfure and nitrogen atoms of ranitidine can be protonated easily, due to high electron density on it, leading to positively charged inhibitor species. The adsorption can occur via electrostatic interaction between positively charged inhibitor molecule and negatively charged metal surface [21, 28] leading to physisorption of the inhibitor molecules. Further, co-ordinate bond may be formed between unshared e- pairs of unprotonated nitrogen atom of the inhibitor and vacant d-orbitals of metal surface atoms. Additionally, inhibitor molecule may be chemically adsorbed due to the interaction of π electrons of the furan ring of the inhibitor with vacant d-orbitals of the metal [32].
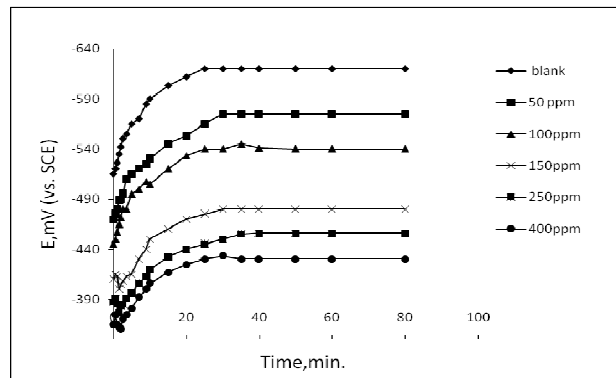
Figure 7. Potential–time curves for carbon steel immersed in 2 M HCl solution in the absence and presence of expired ranitidine.

Open circuit potential measurements

The potential of mild steel electrodes immersed in 1 M HCl solution was measured as a function of immersion time in the absence and presence of expired ranitidine, as shown in Fig. 7. It is clear that the potential of mild steel electrode immersed in 1 M HCl solution (blank curve) tends towards more negative potential firstly, giving rise to short step. This behavior was reported by another investigator [40]. It represents the breakdown of the pre-immersion air formed oxide film present on the surface, according to the following equation:

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
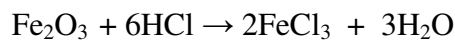
This is followed by the growth of a new oxide film inside the solution, so that the potential was shifted again to more noble direction until steady state potential is established. Addition of inhibitor molecules to the aggressive medium produces a negative shift in the open circuit potential due to the retardation of the cathodic reaction.
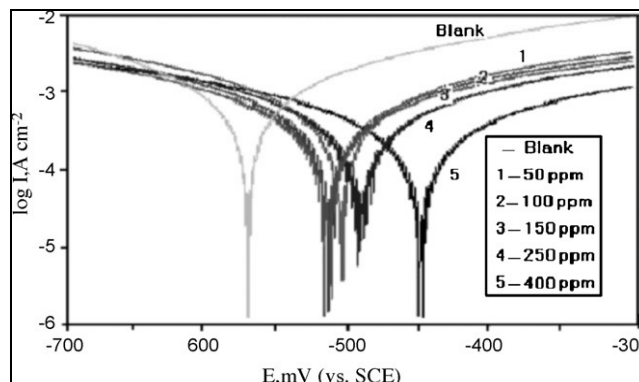

Figure 8. Potentiodynamic polarization curves of mild steel in 1 M HCl solution at 30 ℃ containing various concentrations of the inhibitor.

Polarization measurements

Polarization curves for mild steel in 1 M hydrochloric acid without and with addition of different concentrations of the inhibitor are shown in Fig. 8. The values of electrochemical parameters associated with polarization measurements, such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), tafel slopes (βa ,βc) and calculated inhibition efficiency (IE%), are listed in Table 4. The inhibition efficiency is given by the following equation [41].

$$I.E.(\%) = 1 - \frac{I_{inh}}{I_{uninh}} \times 100 \qquad (8)$$

where I_{uninh} and I_{inh} are the corrosion current densities in the absence and presence of the inhibitor, respectively.

Table 4. Electrochemical parameters of mild steel in 1 M hydrochloric acid solution at 303 K.

inhibitor concentration (ppm)	i_{corr} mA/cm^2	- E_{corr} mV	Ba mV/decade	Bc mV/decade	I.E(%)
blank	282	549	89	128	-
50ppm	105	533	87	126	62
100ppm	93	498	86	125	76
150ppm	72	486	83	119	80
250ppm	59	473	82	117	86
400ppm	38	462	81	115	90

Corrosion current density decreased noticeably with increase in inhibitor concentration, indicating the increased inhibition efficiency with the increase in the concentration of the inhibitor. Generally, in acidic solution the anodic process of corrosion is the passage of metal ions from the solid metal to the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen molecules or reduction of oxygen. In the present study, the corrosion potential values slightly shifted to more positive values, indicating that the addition of inhibitor molecule reduces both anodic dissolution and cathodic reduction; therefore, ranitidine hydrochloride could be classified as a mixed type inhibitor, but the anodic effect is more pronounced.

The anodic and cathodic Tafel constants did not change significantly with increase in inhibitor concentration, suggesting that the presence of the inhibitor does not alter the reaction mechanism, and that the inhibition effect has occurred due to simple blocking of the active sites, thereby reducing available surface area of the corroding metal.

Electrochemical impedance spectroscopic measurements (EIS)
Impedance spectra (Nyquist plots) of mild steel in 1 M HCl containing various concentrations of the inhibitor at 30 °C are shown in Fig. 9. Nyquist plots contain depressed semicircles with the centre under the real axis. The size of the semicircle increases with the inhibitor concentration, indicating the charge transfer process as the main controlling factor of the corrosion of mild steel. It is apparent from the plots that the impedance of the inhibited solution has increased with the increase in the concentration of the inhibitor. The experimental results of

EIS measurements for the corrosion of mild steel in 1 M HCl in the absence and presence of inhibitor are given in Table 5.
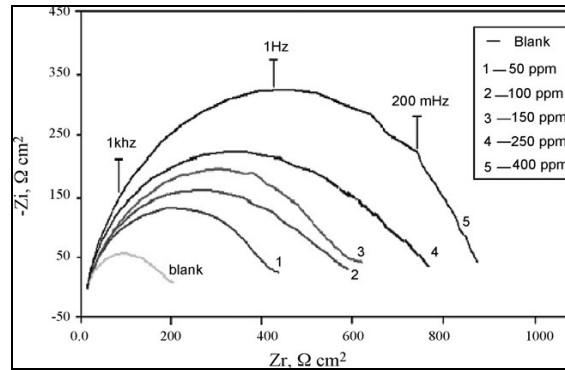

Figure 9. Nyquist plots for mild steel in 1 M HCl solution at 30 ºC containing various concentrations of the inhibitor.

Table 5. AC impedance data of mild steel in 1 M HCl solution at 30 ºC.

inhibitor concentration (ppm)	R_p (Ω cm^2)	Cdl (μ Fcm^{-2})	I.E %
blank	174	142	-
50ppm	421	58	60
100ppm	603	41	75
150ppm	642	36	81
250ppm	776	29	88
400ppm	932	25	92

It can be observed that polarization resistance (Rp) value increased with increase in the concentration of the inhibitor, whereas values of the capacitance of the interface (C_{dl}) start decreasing, with increase in inhibitor concentration, which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor acts via adsorption at the metal/solution interface [42] and the decrease in the C_{dl} values is caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the electrode surface, which decreases the extent of metal dissolution [43].

The inhibition efficiency [44] is given by equation (9)

$$IE (\%) = (Rp\ inhi) - Rp)/(Rp(inhi)) \times 100 \qquad (9)$$

where R_p is the polarization resistance without inhibitor, and R_p(inhi) is the polarization resistance with inhibitor.

C_{dl} value is obtained from equation (10):

$$\omega_{max} = 2\pi f_{max} = \frac{1}{RpCdl} \qquad (10)$$

where f_{max} is the frequency at the top of the semicircle (where-Z'' is maximum).

Conclusions

1) Results obtained from the experimental data show that expired ranitidine hydrochloride is a good inhibitor for the corrosion of mild steel in 1M HCl and inhibition efficiency was more pronounced with increase in the inhibitor concentration.

2) The inhibition efficiency decreased with increase in temperature, leading to the conclusion that the protective film of the compounds formed on the mild steel surface is less stable at higher temperature.

3) The values of ΔG_{ads} indicate adsorption of the inhibitor by both physical and chemical process.

4) The potentiodynamic polarization curves imply that expired ranitidine hydrochloride acts as a mixed type inhibitor, but under prominent anodic control, for corrosion of mild steel in 1 M HCl.

5) The adsorption of inhibitor on the mild steel surface obeys Langmuir adsorption isotherm.

6) The polarization resistance (R_p) value increased with increase in the concentration of the inhibitor.

7) Results obtained from polarization, EIS and weight loss measurements are in good agreement with each other.

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