Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/molliq

# Synthesis and application of new acetohydrazide derivatives as a corrosion inhibition of mild steel in acidic medium: Insight from electrochemical and theoretical studies



M. Yadav<sup>a,\*</sup>, R.R. Sinha<sup>a</sup>, S. Kumar<sup>a</sup>, I. Bahadur<sup>b,c,\*</sup>, E.E. Ebenso<sup>b,c</sup>

<sup>a</sup> Department of Applied Chemistry, Indian School of Mines, Dhanbad 826004, India

<sup>b</sup> Material Science Innovation & Modelling (MaSIM) Research Focus Area, Faculty of Agriculture, Science and Technology, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735. South Africa

<sup>c</sup> Department of Chemistry, North-West University (Mafikeng Campus), Private Bag X2046, Mmabatho 2735, South Africa

# ARTICLE INFO

Article history: Received 6 April 2015 Accepted 3 May 2015 Available online xxxx

Keywords: Mild steel Acetohydrazides Corrosion inhibition EIS Polarization Density functional theory

# ABSTRACT

Corrosion inhibition of mild steel in 15% HCl solutions by synthesized acetohydrazides namely, N'-[(1Z)-phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and N'-[(1Z)-4-chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA) was studied using chemical (weight loss) and electrochemical (potentiodynamic and electrochemical impedance spectroscopy) measurements. It was shown that PQA and CPQA act as good corrosion inhibitor for mild steel protection. It was concluded that the inhibition efficiencies increased with increase in the concentrations of the inhibitor. Tafel polarization studies showed that both the studied inhibitors act as mixed type inhibitor. The high inhibition efficiencies were attributed to the simple blocking effect by adsorption of inhibitor molecules on the steel surface. Atomic Force Microscope (AFM), Scanning Electron Microscope (SEM) and Energy Dispersion X-ray Spectroscopy (EDX) observations confirmed the existence of an absorbed protective film on the metal surface. The density functional theory (DFT) was employed for theoretical calculations and the obtained results were found to be consistent with the experimental findings.

© 2015 Published by Elsevier B.V.

# 1. Introduction

Acethydrazide is an important organic intermediate which is mainly used for the synthesis of nifuratrone in the pharmaceutical industry. Substituted pyrazolones can be prepared by treatment with corresponding hydrazide as strong alkalies [1] with hydrazide and its derivatives were used as versatile synthons. Hydrazides are found to be more reactive functional groups routinely used in protein and carbohydrate chemistry [2,3] and it is also reported that oligonucleotides can be modified with hydrazide [4].

Hydrochloric acid is widely used for pickling, cleaning and descaling of steel and ferrous alloys. The addition of corrosion inhibitors effectively secures the metal against an acid attack. Inhibitors are generally used in these processes to control metal dissolution. Most of the effective corrosion inhibitors are organic compounds containing nitrogen, oxygen, sulfur, aromatic rings and  $\pi$ -electrons in their structures [5–8]. The presence of atoms such as N, O and S in heterocyclic compounds determines both the efficiency and adsorption mechanism [9–14]. The molecular structure of these compounds plays an important role in

\* Corresponding authors.

E-mail addresses: yadavdrmahendra@yahoo.co.in (M. Yadav),

bahadur.indra@gmail.com (I. Bahadur).

determination of their inhibitive performance. Although, the protection mechanism of organic corrosion inhibitors has not been clearly understood [15], it is generally accepted that the corrosion inhibition is achieved due to the interactions between inhibitor molecules and the metal surface; resulting in formation of an inhibitive surface film [9, 10,16,17]. The organic inhibitors decrease the corrosion rate by adsorbing on the metal surface and blocking the active sites by displacing water molecules and forming a compact barrier film on the metal surface. Most of the organic inhibitors are toxic, highly expensive and environment unfriendly. Research activities in recent times are geared towards developing the cheap, non-toxic and environment friendly corrosion inhibitors. A large number of organic compounds including heterocyclic compounds [18–23] were studied as corrosion inhibitors for mild steel [24–26].

The aim of this research is to study the corrosion inhibition effect of two synthesized compounds namely N'-[(1Z)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and N'-[(1Z)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA) on mild steel in 15% HCl solution by using weight loss measurement, electrochemical methods and theoretical calculations. Two derivatives of acetohydrazide have been chosen to discuss the effect of electron withdrawing (-Cl) substituent on inhibition efficiency of the inhibitor. To the best of our knowledge there is no any open literature pertaining on the studied compounds as a corrosion inhibitor on mild steel in



Scheme 1. Synthetic route of N'-[(1Z)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and N'-[(1Z)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA).

acidic medium. The present work is a continuation of our systematic studies on corrosion inhibitor of organic compounds [27–29].

# 2. Experimental

# 2.1. Synthesis of corrosion inhibitors

The compounds PQA and CPQA were synthesized by reported method [30] as shown in Scheme 1. The purity of the compound was checked by thin layer chromatography (TLC) and structure of the compounds was confirmed by using physic-chemical studies. The melting point, yield and IR data of the synthesized compounds are given below:

PQA: Yield 70%, m.p. 105 °C; IR (KBr) cm<sup>-1</sup>: 3470 (N–H, CONH), 1674 (C = N), 1080 (C–O–C), 1181 (N–N), <sup>1</sup>H NMR (DMSO d6)  $\delta$ : 8.17 (s, 1H, CONH), 7.61 (m, 11H, ArH), 7.41 (s, 1H, N = CH), 4.98 (s, 2H, OCH2); Anal. Calcd. for C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 70.71; H, 4.84; N, 13.72. Found: C, 70.81; H, 4.92; N, 13.77%.

CPQA: Yield 70%, m.p. 132 °C; IR (KBr) cm<sup>-1</sup>: 3455 (N–H, CONH), 1670 (C = O), 1624 (C = N), 1065 (C–O–C), 1188 (N–N), 754 (C–Cl); <sup>1</sup>H NMR (DMSO d6)  $\delta$ : 8.25 (s, 1H, CONH), 7.41 (d, 2H, Ar–H near Cl), 7.11 (s, 1H, N = CH), 4.71 (s, 2H, OCH<sub>2</sub>); Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>Cl: C, 63.55; H, 4.07, N, 12.34. Found: C, 63.62; H, 4.12; N, 12.37%.

The structure of inhibitors namely: N'-[(1Z)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and N'-[(1Z)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA) are given in Fig. 1.

# 2.2. Material and methods

#### 2.2.1. Mild steel samples

Mild steel specimens of size 6.0 cm  $\times$  2.5 cm  $\times$  0.1 cm and 1.0 cm  $\times$  1.0 cm  $\times$  0.1 cm with composition (w%) C, 0.14; Mn, 0.98; Si, 0.033; S, 0.018; P, 0.026; Cr, 0.02 and remainder iron were employed



N'-[(1Z)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA)



N'-[(1Z)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA)

Fig. 1. Structure of N'-[(1Z)-Phenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (PQA) and N'-[(1Z)-4-Chlorophenylmethylene]-2-(quinolin-8-yloxy) acetohydrazide (CPQA).

Table 1	
Corrosion parameters of mild steel in 15% HCl solution in the presence and absence of different inhibitors at different temperatures, obtained from weigh	t loss measurements.

Conc. (ppm)	303 K			313 K			323 K			333 K		
	$CR (mm y^{-1})$	θ	η%									
Blank CPQA	28.2	-	-	58.1	-	-	98.9	-	-	144.5	-	-
50	8.70	0.691	69.13	19.56	0.663	66.33	37.37	0.622	62.21	62.64	0.566	56.65
100	6.32	0.776	77.58	14.47	0.750	75.08	27.74	0.719	71.95	46.64	0.677	67.72
200	4.51	0.840	84.02	10.79	0.814	81.42	21.54	0.782	78.22	38.40	0.734	73.42
300	2.46	0.912	91.25	6.17	0.893	89.38	14.36	0.855	85.48	26.97	0.813	81.33
400	1.63	0.942	94.21	4.30	0.925	92.59	9.43	0.904	90.46	19.34	0.866	86.61
PQA												
50	7.75	0.725	72.52	17.59	0.697	69.72	33.55	0.660	66.07	57.84	0.599	59.9
100	5.62	0.800	80.06	12.94	0.777	77.72	25.81	0.739	73.90	44.69	0.691	69.07
200	3.42	0.887	87.84	8.15	0.859	85.97	17.70	0.821	82.10	32.97	0.772	77.18
300	1.88	0.933	93.32	5.17	0.911	91.10	12.98	0.867	86.87	24.53	0.830	83.02
400	1.35	0.952	95.18	3.50	0.939	93.97	9.17	0.907	90.72	17.80	0.876	87.68

for the weight loss and electrochemical studies respectively. The specimens were abraded using emery papers of different grit sizes up to 1200 grit, polished with  $Al_2O_3$  (1  $\mu$ m and then 0.3  $\mu$ m particle size), washed with tap water followed by distilled water, degreased with acetone, dried and stored in desiccator.

# 2.2.2. Test solution

The test solution was prepared by dilution of AR grade HCl with double-distilled water. The concentration range of inhibitors employed was varied from 100 to 300 ppm (mg  $L^{-1}$ ). For weight loss and electrochemical studies 500 mL and 150 mL volume of the test solution were used.

#### 2.2.3. Weight loss measurements

Weight loss measurements were performed in the absence and presence of different concentrations (100 to 300 ppm) of inhibitors at different temperatures (303 K–333 K) according to the standard methods [19]. The corrosion rate (*CR*), inhibition efficiency ( $\eta$ %) and surface coverage ( $\theta$ ) were determined by following equations [31]:

$$CR(\text{mm } \text{y}^{-1}) = \frac{8.76 \times 10^4 \times W}{D \times A \times t}$$
(1)



**Fig. 2.** Arrhenius plots of log *CR* versus 1000/*T* for mild steel corrosion in 15% HCl solution (a) PQA, (b) CPQA.

#### Table 2

Activation parameter for mild steel in 15% HCl solution in the absence and presence of inhibitor obtained from weight loss measurements.

Inhibitor	Concentration (ppm)	$E_{\rm a}$ (kJ mol <sup>-1</sup> )	$\Delta H^*(kJ/mol)$	$\Delta S^*(\text{J mol}^{-1}\text{ K}^{-1})$
Blank	-	45.78	43.13	-74.45
PQA	50	56.17	53.53	-51.10
	100	58.14	55.50	-47.27
	200	63.75	61.10	-33.10
	300	72.56	69.94	-9.47
	400	73.14	70.51	-8.78
CPQA	50	55.29	52.65	-53.01
	100	55.95	53.30	-53.58
	200	59.94	57.25	-43.24
	300	67.53	64.88	-23.33
	400	69.00	66.36	-21.80

where, W = weight loss (g), A = area of specimen (cm<sup>2</sup>) exposed in acidic solution, t = exposure time (h), and D = density of mild steel (g · cm<sup>-3</sup>).

$$\theta = \frac{CR_0 - CR_i}{CR_0} \tag{2}$$

$$\eta(\%) = \frac{CR_0 - CR_i}{CR_0} \times 100 \tag{3}$$



**Fig. 3.** Transition state plot of log *CR/T* versus 1000/*T* for mild steel in 15% HCl solution at different concentrations of (a) PQA, (b) CPQA.

3.10

3.15

 $1000/T (K^{-1})$ 

3.25

3.20

3.30

.

•

3.00

-2.0

-2.4

100 ppm

200 ppm

300 ppm

400 ppm

3.05



**Fig. 4.** Langmuir plots of  $(C_{inh}/\theta)$  versus  $C_{inh}$  for (a) PQA, (b) CPQA.

where,  $CR_0$  and  $CR_i$  are corrosion rate in the absence and presence of inhibitors. This experiment was repeated at different temperatures of 30, 40, 50 and 60 °C by using water circulated Ultra thermostat to determine the temperature dependence of the inhibition efficiency.

#### 2.2.4. Potentiodynamic polarization measurements

Potentiodynamic polarization measurements were carried out using a computerized electrochemical analyzer model CHI 760D, manufactured by CH Instruments, Austin, USA. The experiments were performed by using of a three electrode cell consisting of mild steel specimen of 1.0 cm<sup>2</sup> working electrode, a platinum counter electrode and a saturated

# Table 3 Adsorption parameters for PQA and CPQA calculated from Langmuir adsorption isotherm for mild steel in 15% HCl solution at a temperature range of 303–333 K.

Inhibitor	Temperature (K)	$K_{ads}$ (M <sup>-1</sup> )	$\Delta G^{\circ}_{ads}$ (kJ mol <sup>-1</sup> )	Slope	$R^2$
PQA	303 K	$7.6\times10^5$	-34.0	0.967	0.992
	313 K	$8.5  imes 10^5$	-34.8	0.972	0.989
	323 K	$9.6 \times 10^{5}$	-35.6	0.981	0.991
	333 K	$1.2  imes 10^4$	-36.0	0.992	0.995
CPQA	303 K	$8.3  imes 10^5$	-33.7	0.974	0.986
	313 K	$9.3  imes 10^5$	-34.6	0.987	0.997
	323 K	$1.0  imes 10^4$	-35.3	0.982	0.995
	333 K	$1.2  imes 10^4$	-35.9	1.014	0.999

calomel electrode (SCE) as reference electrode, designed specifically for potentiodynamic polarization measurements. A luggin capillary arrangement filled with the same tested solution was used to keep the reference electrode close to the working electrode. Potentiodynamic polarization curves were obtained in the potential range from –250 to +250 mV vs. SCE at OCP at a scan rate of 1 mV s<sup>-1</sup>. The linear Tafel segments of anodic and cathodic curves were extrapolated to obtain corrosion current densities ( $i_{corr}$ ) [32,33]. The percentage inhibition efficiency ( $\eta$ %) was calculated using the equation

$$\eta(\%) = \frac{i_{\rm corr}^0 - i_{\rm corr}}{i_{\rm corr}^0} \times 100$$
(4)

where,  $i_{corr}^0$  and  $i_{corr}$  are the values of corrosion.

#### 2.2.5. Electrochemical impedance measurements

Electrochemical impedance measurements were carried out using the same electrochemical cell and electrochemical workstation as used for potentiodynamic polarization measurements in the frequency range from 10 mHz to 100 kHz using amplitude of 10 mV peak to peak with an ac signal at the open-circuit potential. The impedance data were obtained using Nyquist and Bode plots. All impedance data were fitted to appropriate equivalent circuits using ZSimpWin.3.21 software. The inhibition efficiency ( $\eta$ %) was calculated from charge transfer



Fig. 5. Potentiodynamic polarization curves for mild steel in 15% HCl solution in the presence and absence of inhibitor at 303 K. (a) PQA, (b) CPQA.

Table 4 Electrochemical parameter and percentage inhibition efficiency ( $\eta$ %) obtained from polarization studies for mild steel in 15% HCl solution in the presence or absence of inhibitor at 303 K.

Conc. (ppm)	Tafel extrapolation data					EIS data					
	$E_{\rm corr}$ (V vs SCE)	$\beta_{\rm a}~({\rm mV~dec^{-1}})$	$\beta_{\rm c} ({\rm mV}{\rm dec}^{-1})$	$I_{\rm corr}$ ( $\mu$ A cm <sup>-2</sup> )	η%	$R_s (\Omega \text{ cm}^2)$	$R_{\rm ct} (\Omega {\rm cm}^2)$	$Y_0 (\mu { m F}  { m cm}^{-2})$	n	$C_{\rm dl} (\mu { m F}{ m cm}^2)$	η%
Blank	-495	103	182	10.0	-	1.02	2.7	483	0.852	168	-
PQA											
50	-448	112	168	2.28	77.2	0.68	11.1	225	0.862	86.8	75.6
100	-447	97	149	2.08	79.3	0.77	14.8	152	0.874	62.2	81.7
200	-439	106	176	1.42	85.8	0.86	23.2	108	0.882	48.1	88.3
300	-443	82	181	1.02	89.7	0.63	30.7	80	0.888	37.4	91.0
400	-440	118	154	0.88	91.2	0.96	43.8	41	0.912	21.5	93.8
CPQA											
50	-451	98	153	3.47	65.3	0.71	8.1	257	0.858	92.5	66.2
100	-449	87	164	2.38	76.2	0.83	11.2	198	0.863	75.6	75.8
200	-446	114	171	1.54	84.6	0.85	18.0	131	0.878	56.1	84.9
300	-441	92	158	1.06	89.2	0.77	29.7	95	0.881	42.7	90.9
400	-434	108	163	0.96	90.4	0.65	32.2	61	0.892	28.4	92.1

resistance values obtained from impedance measurements using the following relation:

$$\eta(\%) = \frac{R_{\text{ct (inh)}} - R_{\text{ct}}}{R_{\text{ct (inh)}}} \times 100$$
(5)

where  $R_{\text{ct(inh)}}$  and  $R_{\text{ct}}$  are charge transfer resistance in the presence and absence of inhibitor respectively. The values of double layer capacitance ( $C_{\text{dl}}$ ) were calculated from charge transfer resistance and CPE parameters ( $Y_0$  and n) using the expression [34]:

$$C_{\rm dl} = \left(Y_0 R_{\rm ct}^{1-n}\right)^{1/n} \tag{6}$$

where  $Y_0$  is CPE constant and n is CPE exponent. The value of n represents the deviation from the ideal behavior and it lies between 0 and 1.

2.2.6. Scanning electron microscopic and energy dispersive spectroscopy analysis

For surface morphological study of the uninhibited and inhibited mild steel samples, SEM and EDX images were recorded using the instrument HITACHI S3400N.

#### 2.2.7. Atomic force microscopy

The AFM images of polished, uninhibited and inhibited mild steel samples were carried out using a Nanosurf Easyscan2 instrument, Model: NT-MDT, Russia; Solver Pro-47.

#### 2.2.8. Quantum chemical study

Complete geometrical optimizations of the investigated molecules are performed using density functional theory (DFT) with the Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) with 6-31G (d, p) basis set is implemented in Gaussian 03 program package [35,36]. Theoretical parameters such as the energies of the highest occupied and lowest unoccupied molecular orbital ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ), energy gap ( $\Delta E$ ) and dipole moment ( $\mu$ ) were determined.

# 3. Results and discussion

#### 3.1. Weight loss measurements

# 3.1.1. Effect of inhibitor concentration and temperature

Corrosion parameters namely, corrosion rate (*CR*), surface coverage ( $\theta$ ) and inhibition efficiency ( $\eta$ %) of mild steel in 15% HCl solution in the absence and presence of different concentrations (50–400 ppm) of inhibitor at different temperatures (303 K–333 K), obtained from weight loss measurements are shown in Table 1. From Table 1, it is apparent

that inhibition efficiency increased with increasing the concentration of the inhibitors. The inhibition efficiency of PQA and CPQA at 400 ppm was found to be 95.1% and 94.2% respectively, at 303 K (Table 1). By increasing the inhibitor concentration, the part of metal



**Fig. 6.** Nyquist plot for mild steel in 15% HCl solution containing various concentrations of (a) PQA, (b) CPQA at 303 K.



Fig. 7. Equivalent circuit applied for fitting of the impedance spectra.

surface covered by inhibitor molecules increases and that leads to an increase in the inhibition efficiencies [37].

It is also clear from Table 1 that the inhibition efficiency decreased with increasing temperature from 303 K to 333 K. Such type of behavior can be described on the basis that the increase in temperature leads to a shift of the equilibrium constant towards desorption of the inhibitor molecules at the surface of mild steel [38]. The inhibition efficiency of PQA is greater than CPQA at all concentrations and temperatures.

#### 3.1.2. Thermodynamic and activation parameters

To evaluate the adsorption and thermodynamic activation parameters of corrosion processes of mild steel in 15% HCl solution, weight loss measurements were carried out in the temperature range 303–333 K in the absence and presence of inhibitors after 6 h of



Fig. 8. Bode plots for mild steel in a 15% HCl solution in the absence and presence of different concentrations of inhibitors (a) PQA, (b) CPQA.

immersion time. The apparent activation energy  $(E_a)$  for dissolution of mild steel in 15% HCl was calculated by using the Arrhenius equation.

$$\log CR = \frac{-E_a}{2.303RT} + \log A \tag{7}$$

where  $E_a$  is the apparent activation energy, R is the molar gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>), T is the absolute temperature (K) and A is the Arrhenius pre-exponential factor. Fig. 2(a, b) presents the Arrhenius plot of log CR against 1/T for the corrosion of mild steel in 15% HCl solution in the absence and presence of inhibitors PQA and CPQA at concentrations ranging from 50 to 400 ppm. From Fig. 2(a, b), the activation energy was calculated using the expression  $E_a = -(\text{slope}) \times 2.303R$ . The calculated values of  $E_a$  are summarized in Table 2. It is evident from Table 2 that the values of the apparent activation energy for the inhibited solutions were higher than that for the uninhibited solution, indicating that the dissolution of mild steel was decreased due to formation of a barrier by the adsorption of the inhibitors on metal surface [39].

The values of standard enthalpy of activation ( $\Delta H^*$ ) and standard entropy of activation ( $\Delta S^*$ ) can be calculated by using the transition state equation:

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right)$$
(8)

where, h is Planck's constant and N is the Avogadro number, respectively.

A plot of log (*CR*/*T*) against 1/*T* (Fig. 3a, b) gave straight lines with a slope of  $-\Delta H^*/2.303R$  and an intercept of  $[\log(R/Nh) + \Delta S^* / (2.303R)]$ , from which the activation thermodynamic parameters  $\Delta H^*$  and  $\Delta S^*$  were calculated, as listed in Table 2. The negative value of  $\Delta S^*$  for both inhibitors indicates that the formation of the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of the transition from reactants to activated complex [40].

#### 3.1.3. Adsorption isotherm

Information on the interaction between the inhibitor molecules and the mild steel surface can be provided by adsorption isotherm. Plotting  $C_{inh}/\theta$  vs.  $C_{inh}$  yielded a straight line (Fig. 4a, b) with a correlation coefficient ( $R^2$ ) and slope values given in Table 3 at different temperatures. The  $R^2$  and slope values in Table 3 are near to unity indicating that the adsorption of these inhibitors obeys the Langmuir adsorption isotherm.

The values of  $K_{ads}$  were calculated from the intercept of Fig. 4(a, b). Large values of  $K_{ads}$  obtained for both studied inhibitors suggesting more efficient adsorption and hence better corrosion inhibition efficiency. Using the values of  $K_{ads}$ , the values of  $\Delta G^{\circ}_{ads}$  were obtained by using the following equation:

$$\Delta G_{\rm ads}^0 = -RT \ln \left( K_{\rm ads} \right) \tag{9}$$

where *R* is the gas constant and *T* is the absolute temperature (K). The value of 55.5 is the concentration of water in solution in mol L<sup>-1</sup>. Calculated values of  $K_{ads}$  and  $\Delta G^{\circ}_{ads}$  are listed in Table 3. The negative values of  $\Delta G^{\circ}_{ads}$  reveal the spontaneity of adsorption process. In general, values of  $\Delta G^{\circ}_{ads}$  up to -20 kJ mol<sup>-1</sup> are compatible with physisorption and those which are more negative than -40 kJ mol<sup>-1</sup> involve chemisorptions [41]. The calculated  $\Delta G^{\circ}_{ads}$  values for PQA and CPQA were found in the range of -34.4 to -36.0 and -33.7 to -35.9 kJ mol<sup>-1</sup>, respectively, at different temperatures (303–333 K), these values were between the threshold values for physical adsorption and chemical adsorption, indicating that the adsorption process of these inhibitors at mild steel surface involves both the physical as well as chemical adsorption. Similar conclusion was also reported by Ozcan [42], who studied the use of cystine as a corrosion inhibitor on mild steel in sulfuric acid.



Fig. 9. SEM image of mild steel in 15% HCl solution after 6 h immersion at 303 K (a) before immersion (polished), (b) after immersion without inhibitor, (c) with 400 ppm PQA, (d) with 400 ppm CPQA.

#### 3.2. Potentiodynamic polarization studies

Potentiodynamic polarization curves of mild steel in 15% HCl containing PQA and CPQA at 303 K are shown in Fig. 5(a, b), respectively. The addition of each compound in acidic medium causes a remarkable decrease in the corrosion rate and shifts the both anodic and cathodic curves to lower current densities. It is clear that the addition of inhibitors hindered the acid attack on the steel electrode and a comparison of curves in both cases, showed that, with respect to the blank, increasing the concentration of the inhibitors gave rise to a consistent decrease in anodic and cathodic current densities indicating that inhibitors act as mixed type inhibitor [43]. Corrosion potential, anodic Tafel slope, cathodic Tafel slope and corrosion current density values are given in Table 4. It is clear from Table 4 that after increasing the concentration of inhibitor, the inhibition efficiency increased, while the corrosion current density decreased due to adsorption of PQA and CPQA on the metal surface. The minor shift in E<sub>corr</sub> value (61 mV) towards positive direction in the presence of inhibitors as compared to the  $E_{\text{corr}}$  value in the absence of inhibitor indicate that PQA and CPQA act as mixed type inhibitor with predominant control of anodic reaction [44].

#### 3.3. Electrochemical impedance spectroscopy studies

Adsorption of a protective inhibitor on the metal surface causes a significant increase in impedance of the corrosion system, thus causing an increase in the resistance to charge transfer process. Therefore, the performance of an inhibitor can be determined by impedance measurements of the corrosion system. The degree of the corrosion protection can be determined by comparing the impedance obtained in the

presence and absence of inhibitors in the corrosive environment. The Nyquist plots for mild steel obtained at mild steel 15% HCl solution interface with and without the different concentrations of PQA and CPQA at 303 K are shown in Fig. 6(a, b). The existence of a depressed semicircle with its center below the axis (Z') in Nyquist plots (Fig. 6a, b) for both inhibitors suggests the non-homogeneity and roughness of the mild steel surface. The EIS spectra of all tests were analyzed using the equivalent circuit shown in Fig. 7, which is a parallel combination of the charge transfer resistance ( $R_{ct}$ ) and the constant phase element (CPE), both in series with the solution resistance ( $R_s$ ). This type of electrochemical equivalent circuit was reported previously to model the iron/acid interface [45]. Constant phase element (CPE) is introduced instead of pure double layer capacitance to give more accurate fit as the double layer at interface does not behave as ideal capacitor.

The electrochemical parameters such as solution resistance, charge transfer resistance and CPE constants ( $Y_0$  and n) obtained from the fitting of the experimental data of Nyquist plots in the equivalent circuit shown in Fig. 6 are presented in Table 4.

The data shown in Table 4 reveal that the value of  $R_{ct}$  increases with addition of inhibitors as compared to the blank solution, the increase in  $R_{ct}$  value is attributed to the formation of a protective film at the metal/solution interface. The  $C_{dl}$  value decreases on increasing the concentration of both the inhibitors, indicating the decrease in local dielectric constant and/or to an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules are adsorbed at the metal/solution interface.

The Bode phase angle plots (Fig. 8a, b) show single maximum (one time constant) at intermediate frequencies, broadening of this maximum in the presence of inhibitors accounts for the formation of a



Fig. 10. EDX spectra of mild steel specimens (a) polished, (b) after immersion without inhibitor, (c) with 400 ppm PQA, (d) with 400 ppm CPQA.

protective layer on the electrode surface. Moreover, there is only one phase maximum in Bode plot (Fig. 8a, b) for both inhibitors, which indicates only one relaxation process, which would be the charge transfer process, taking place at the metal–electrolyte interface.

Fig. 8(a, b) shows that the impedance value in the presence of both inhibitors is larger than in the absence of inhibitors and the value of impedance increases on increasing the concentration of both studied inhibitors. These mean that the corrosion rate is reduced in the presence of the inhibitors and continued to decrease on increasing the concentration of inhibitors. Electrochemical results ( $\eta$ %) are in good agreement with the results ( $\eta$ %) obtained by weight loss experiment.

 Table 5

 Percentage atomic contents of elements obtained from EDX spectra.

Inhibitors	Fe	С	S	Cr	Mn	Cl	Ν	0
Polished mild steel	85.26	12.46	-	0.86	0.46	-	-	-
Mild steel in blank HCl	83.12	15.68	-	0.67	0.28	2.29	-	6.36
Mild steel in CPQA	74.12	18.15	1.72	0.56	-	0.36	5.36	15.35
Mild steel in PQA	71.25	19.72	1.68	0.54	-	0.31	5.24	15.26

#### 3.4. Scanning electron microscopy

SEM photomicrographs for mild steel in 15% HCl solution in the absence and presence of 400 ppm of PQA and CPQA are shown in Fig. 9(a–d). The morphology of the polished mild steel specimen (Fig. 9a) is very smooth and shows no corrosion while mild steel specimen dipped in 15% HCl solution in the absence of inhibitor (Fig. 9b) is very rough and the surface is damaged due to metal dissolution. However, the presence of 400 ppm of inhibitor suppresses the rate of corrosion and surface damage has been diminished considerably (Fig. 9c, d) as compared to the blank solution (Fig. 9b) suggesting formation of a protective inhibitor film at the mild steel surface.

#### 3.5. Energy dispersive spectroscopy

Energy dispersive X-ray analysis (EDX) technique was employed in order to get information about the composition of the surface of the mild steel sample in the absence and presence of inhibitors in 15% HCl solution. The results of EDX spectra are shown in Fig. 10(a–d). The percentage atomic content of various elements of the polished, uninhibited and inhibited mild steel surface determined by EDX is shown in Table 5. The percentage atomic content of Fe for mild steel immersed in 15% HCl



Fig. 11. Atomic force micrographs of mild steel surface (a) polished mild steel, (b) mild steel in 15% HCl solution and (c) in the presence of inhibitor CPQA (d) PQA.

solution is 83.12%, and those for mild steel dipped in an optimum concentration (400 ppm) of CPQA and PQA are 74.12% and 71.25%, respectively. From Fig. 10(a–d) it is apparent that the spectra of inhibited samples show suppressed Fe peaks, when compared with the polished and uninhibited mild steel sample. This suppression of Fe lines is due to the inhibitory film formed on the mild steel surface. The EDX spectra of inhibited mild steel contains the peaks corresponding to all the elements present in the inhibitor molecules indicating the adsorption of inhibitor molecules at the surface of mild steel.

# 3.6. Atomic force microscopy

The three-dimensional AFM images of polished, uninhibited and inhibited mild steel samples are shown in Fig. 11(a-d). The average roughness values of polished mild steel sample (Fig. 11a) and mild steel sample in 15% HCl solution without inhibitor (Fig. 11b) were found as 25 and 650 nm. It is clearly shown in Fig. 11(b) that mild steel sample is badly damaged due to the acid attack on surface. However, in the presence of optimum concentration (400 ppm) of CPQA



Fig. 12. The optimized structure (left) and HOMO (center) and LUMO (right) distribution for molecules (a) CPQA, (b) PQA [Atom legend: white = H; gray = C; blue = N; red = O].

Table 6	
Quantum chemical parameters for different inhibitors.	
	_

Inhibitor	$E_{\rm HOMO}~({\rm eV})$	$E_{\text{LUMO}}$ (eV)	$\Delta E (eV)$	$\mu$ (D)
PQA	-5.040	-1.651	3.389	4.32
CPQA	-5.899	-1.526	4.373	3.66

and PQA as shown in Fig. 11(c, d), the average roughness values were reduced to 88 and 75 nm, respectively. The lower value of roughness for PQA than CPQA reveals that PQA protects the mild steel surface more efficiently than CPQA in 15% HCl solution.

# 3.7. Theoretical calculation

The optimized structure,  $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$  for CPQA and PQA are shown in Fig. 12(a, b). The quantum chemical parameters such as the energy of the highest occupied molecular orbital ( $E_{\text{HOMO}}$ ), the energy of the lowest unoccupied molecular orbital ( $E_{\text{LUMO}}$ ), energy gap ( $\Delta E$ ) and dipole moment ( $\mu$ ) were determined and summarized in Table 6. According to the frontier molecular orbital (FMO) theory of chemical reactivity, the formation of a transition state is due to interaction between HOMO and LUMO of reacting species. The smaller the orbital energy gap ( $\Delta E$ ) between the participating HOMO and LUMO, the stronger the interactions between two reacting species [46].

It was reported previously by some researchers that smaller values of  $\Delta E$  and higher values of dipole moment ( $\mu$ ) are responsible for higher inhibition efficiency [47]. The lower values of the energy gap  $\Delta E$  will render good inhibition efficiencies since the energy to remove an electron from the last occupied orbital will be minimized. According to HSAB theory hard acids prefer to co-ordinate to hard bases and soft acid to soft bases. Fe is considered as soft acid and will co-ordinate to molecule having maximum softness and small energy gap ( $\Delta E =$  $E_{\text{LUMO}} - E_{\text{HOMO}}$ ). From Table 6 it is clear that the highest value of  $E_{\text{HOMO}}$  (-5.04 eV),  $\mu$  (4.32 D) and lowest values of  $\Delta E$  (3.389 eV) and  $E_{\text{LUMO}}$  (-1.651 eV) are found for PQA, indicating that PQA has more potency to get adsorbed on the mild steel surface resulting greater inhibition tendency than CPQA. Literature reveals that the use of Mulliken population and HOMO population analysis can be used for the determination of possible adsorption centers of the inhibitors [48–50]. The generalized interpretation given by several authors is that the higher is the magnitude and the number of negatively charged heteroatom present in an inhibitor molecule, the higher is its ability to be adsorbed on the metal surface via a donor–acceptor type bond [49] and the more negatively charged regions with major distribution of the HOMO are also interpreted as possible centers of adsorption. Mulliken charges according to the numeration of corresponding atoms are shown in Fig. 13(a, b). It is evident from Fig. 13(a, b) that both inhibitors had a considerable excess of negative charge around the nitrogen atoms, oxygen atoms, indicating that these are the coordinating sites of the inhibitors.

# 3.8. Mechanism of inhibition

Corrosion inhibition of mild steel in 15% hydrochloric acid solution by both inhibitors (PQA and CPQA) can be explained on the basis of molecular adsorption. These compounds inhibit corrosion by controlling both anodic as well as cathodic reactions. In 15% hydrochloric acid solutions these inhibitors exist as protonated species. In both inhibitors the nitrogen atoms present in the molecules can be easily protonated in acidic solution and convert into quaternary compounds. These protonated species adsorbed on the cathodic sites of the mild steel and decrease the evolution of hydrogen. The adsorption on anodic site occurs through  $\pi$ -electrons of quinoline and phenyl rings and lone pair of electrons of nitrogen and oxygen atoms present in both the inhibitors which decrease the anodic dissolution of mild steel.

#### 4. Conclusions

The synthesized acetohydrazide derivatives showed good inhibition efficiencies for the corrosion of mild steel in 15% HCl solution and the inhibition efficiency increased on increasing the concentration of inhibitor. The inhibiting performance of PQA is better than CPQA.



Fig. 13. The Mulliken charge density of (a) CPQA, (b) PQA.

- Polarization studies showed that both tested inhibitors are mixed type in nature.
- > EIS measurements show that charge transfer resistance ( $R_{ct}$ ) increases and double layer capacitance ( $C_{dl}$ ) decreases in the presence of inhibitors, suggested the adsorption of the inhibitor molecules on the surface of mild steel.
- The results obtained from SEM, EDX, AFM and Langmuir adsorption isotherm suggested that the mechanism of corrosion inhibition is occurring mainly through adsorption process.
- ➤ Quantum chemical results of PQA and CPQA showed higher value of  $E_{\text{HOMO}}$ , lower value of  $E_{\text{LUMO}}$ , and smaller value of  $\Delta E$ , indicating that both inhibitors are good corrosion inhibitor for mild steel in 15% HCl solution.

#### Acknowledgments

The authors acknowledge funding from North-West University and Department of Science and Technology and the National Research Foundation (DST/NRF) South Africa grant funded (Grant UID: 92333) for postdoctoral scholarship of Dr. I. Bahadur.

#### References

- [1] P.E. Gagnon, B. Nolin, R.N. Jones, Can. J. Chem. 29 (1951) 843-847.
- [2] S. Raddatz, J. Mueller-Ibeler, J. Kluge, L. Wab, G. Burdinski, J.R. Havens, T.J. Onofrey, D.G. Wang, M. Schweitzer, Nucleic Acid Res. 21 (2002) 4793–4802.
- [3] G.T. Hermanson, Bioconjugate Techniques, Academic Press, San Diego, 1996.
   [4] T.D. Lumley-Woodyear, C.N. Campbell, A. Heller, J. Am. Chem. Soc. 118 (1996) 5504–5505.
- [5] K.C. Emregul, O. Atakol, Mater. Chem. Phys. 83 (2004) 373-379.
- [6] H.A. Sorkhabi, B. Shaabani, D. Seifzadeh, Electrochim. Acta 50 (2005) 3446–3452.
   [7] M. Hosseini, S.F.L. Mertens, M. Ghorbani, R.M. Arshadi, Mater. Chem. Phys. 78 (2003)
- 800-808.
- [8] H. Keles, M. Keles, I. Dehri, O. Serindag, Colloids Surf. 320 (2008) 138-145.
- [9] M.M. Antonijevic, M.B. Petrovic, Int. J. Electrochem. Sci. 3 (2008) 1–28.
   [10] J.O. Bockris, A.K.N. Reddy, Modern Electrochemistry, second ed. Kluwer Academic/
- Plenum Publishers, New York, 2000.
- [11] A. Popova, E. Sokolova, S. Raicheva, M. Christov, Corros. Sci. 45 (2003) 33–58.
- [12] N.C. Subramanyam, B.S. Sheshadri, S.M. Mayanna, Corros. Sci. 34 (1993) 563–571.
   [13] A. Kokalj, S. Peljhan, M. Finsgar, I. Milosev, J. Am. Chem. Soc. 132 (2010) 16657–16668.
- [14] F. Touhami, A. Aouniti, S. Kertit, Y. Abed, B. Hammouti, A. Ramdani, K. Elkacemi, Corros. Sci. 42 (2000) 929–940.

- [15] A. Kokalj, Electrochim. Acta 56 (2010) 745–755.
- [16] V. Sastri, Corrosion Inhibitors: Principles and Applications, John Wiley & Sons, Inc., Hoboken, New Jersey, 2011.
  - [17] S.N. Raicheva, E.I. Sokolova, Russ. J. Electrochem. 42 (2006) 213-1223.
  - [18] E.E. Ebenso, U.J. Ekpe, B.I. Ita, O.E. Offiong, U.J. Ibok, Mater. Chem. Phys. 60 (1999) 79–90.
  - [19] K.S. Jacob, G. Parameswaran, Corros. Sci. 52 (2010) 224-228.
  - [20] E.A. Noor, Corros. Sci. 47 (2005) 33–55.
  - [21] M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre, F. Bentiss, Corros, Sci. 47 (2005) 485–505.
  - [22] F. Bentiss, M. Bovanis, B. Mernari, M. Traisnel, H. Vezin, M. Lagrenee, Appl. Surf. Sci. 253 (2007) 3696–3704.
  - [23] Z. Ait, D. Chebabe, A. Dharmraj, N. Hajjaji, A. Srhirri, M.F. Montemor, M.G.S. Ferreira, A.C. Bastos, Corros. Sci. 47 (2005) 447–459.
  - [24] M. Lagrenee, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, Corros. Sci. 44 (2002) 573–588.
  - [25] R. Solmaz, Corros. Sci. 52 (2010) 3321-3330.
  - [26] J. Aljourani, K. Raeissi, M.A. Golozar, Corros. Sci. 51 (2009) 1836-1843.
  - [27] M. Yadav, D. Sharma, S. Kumar, S. Kumar, I. Bahadur, E.E. Ebenso, Int. J. Electrochem. Sci. 9 (2014) 6580–6593.
  - [28] M. Yadav, S. Kumar, N. Kumari, I. Bahadur, E.E. Ebenso, Int. J. Electrochem. Sci. 10 (2015) 602–624.
  - [29] M. Yadav, S. Kumar, I. Bahadur, D. Ramjugernath, Int. J. Electrochem. Sci. 9 (2014) 6529–6550.
  - [30] M. Ahmed, R. Sharma, D.P. Nagda, J.L. Jat, G.L. Talesara, ARKIVOC 1442 (2006) 66–75.
  - [31] G. Shukla, S.K. Dwivedi, P. Sundaram, S. Prakash, Ind. Eng. Chem. Res. 50 (2011) 1954–11959.
  - [32] E. McCafferty, Corros. Sci. 47 (2005) 3202-3215.
  - [33] M.A. Amin, K.F. Khaled, S.A. Fadl-Allah, Corros. Sci. 52 (2010) 140–151.
  - [34] A.R.S. Priya, V.S. Muralidharam, A. Subramania, Corrosion 64 (2008) 541–552.
  - [35] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785-789.
  - [36] A.D. Becke, J. Chem. Phys. 98 (1993) 1372-1377.
  - [37] S.S. Abdel-Rehim, M.A.M. Ibrahim, K.F. Khaled, J. Appl. Electrochem. 29 (1999) 593–599.
  - [38] L. Fragoza-Mar, O. Olivares-Xometl, M.A. Domínguez-Aguilar, E.A. Flores, P. Arellanes-Lozada, F. Jimenez-Cruz, Corros. Sci. 61 (2012) 171–184.
  - [39] I. Dehri, M. Ozcan, Mater. Chem. Phys. 98 (2006) 316-323.
  - [40] X. Wang, H. Yang, F. Wang, Corros. Sci. 53 (2011) 113-121.
  - [41] M. Behpour, S.M. Ghoreishi, N. Soltani, M. Salavati-Niasari, M. Hamadanian, A. Gandomi, Corros. Sci. 50 (2008) 2172–2181.
  - [42] M.J. Ozcan, Solid State Electrochem. 12 (2008) 1653-1661.
  - [43] C. Cao, Corros. Sci. 38 (1996) 2073–2082.
  - [44] H. Amar, A. Tounsi, A. Makayssi, A. Derja, J. Benzakour, A. Outzourhit, Corros. Sci. 49 (2007) 2936–2945.
  - [45] E.E.F. El-Sherbini, S.M. Abdel Wahaab, M. Deyab, Mater. Chem. Phys. 89 (2005) 183-191.
  - [46] S. Xia, M. Qiu, L. Yu, L. Liu, H. Zhao, Corros. Sci. 50 (2008) 2021–2029.
  - [47] V.S. Sastri, J.R. Perumareddi, Corrosion 53 (1997) 617-622.
  - [48] N.K. Allam, Appl. Surf. Sci. 253 (2007) 4570-4577
  - [49] G. Bereket, C. Ögretir, C. Ozsahim, J. Mol. Struct. 663 (2003) 39-46.
  - [50] J. Fang, J. Li, J. Mol. Struct. 593 (2002) 179-185.