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Organic nanoparticles of acetohydrazides as novel inhibitors for mild steel corrosion

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Abstract

Novel organic nanoparticles (ONPs) of (E)-2-(4-(hydrazonomethyl)phenoxyl) acetohydrazide (H2) and N'((E)-benzylidene)-2-(4-((E) hydrazonomethyl)phenoxyl) acetohydrazide (H3) were prepared by re-precipitation method. The ONPs were characterized by MS, ¹H-NMR, ¹³C-NMR, FT-IR, DLS, TEM and XRD. Both nanoparticles revealed a semispherical shape with a particle size of 3.0 nm and 2.0 nm for H2 and H3 nanoparticles, respectively. The protective effect of ONPs on Mild steel in 1.0 M HCl was monitored by polarization, electrochemical impedance spectroscopy (EIS), scanning electron microscope (SEM) and atomic force microscopy (AFM). The obtained results revealed that the inhibition efficiency increased with the inhibitor concentration increment. Maximum inhibition efficiencies at a constant concentration of 1x10⁻³ M were 88.2% and 96.7% for H2 and H3, respectively. The inhibition mechanism depended on the physical adsorption of nanoparticles on steel surface which was confirmed by SEM, AFM and impedance results. These novel nanomaterials showed great anti-corrosion behavior and thus can be potentially used in industrial applications such as cooling water systems, pipes, and oil production units.

Key words: Organic nanoparticles; Corrosion inhibition; Mild steel; EIS; SEM/AFM.

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Introduction

Despite their high fabrication cost, metals are commonly used in various industrial applications due to their unique properties. However, the major limitation of using such materials is that they undergo corrosion when exposed to harsh environments which significantly reduces their life span. Corrosion is an electrochemical phenomenon that converts metals to a more stable states upon exposure to some corrosive media¹

Mild steel is highly abundant and has prime mechanical properties, therefore, it is used as a building material in many chemical and petrochemical applications². However, mild steel has a limited resistance to corrosion under drastic conditions, including exposure to hydrochloric acid (HCl) which is used in many processes and causes serious corrosion on mild steel³. Recently, the use of organic inhibitors is considered an effective method for protecting steel from corrosion⁴⁻⁶. Organic compounds are utilized as corrosion retardants for mild steel and iron because of their ability to minimize corrosion in different corrosive media^{7, 8}. Generally, theses organic compounds (heterocyclic compounds) have been utilized as efficient corrosion inhibitors due to their high adsorption on metallic surfaces through the presence of π and non-bonding electrons, aromatic rings and polar functional moieties, which behave as adsorption centers^{9, 10}.

Organic inhibitors can adsorb onto the metal/solution interface via four distinct mechanisms: (a) electrostatic attraction between charged inhibitor and the metal; (b) interaction between uncharged electron pairs in the inhibitor and the metal; (c) interaction between π -electrons and the metal and (d) a combination of mechanism (a) and (c)^{11, 12}. Such organic inhibitors usually contains heteroatoms with electronegative functional groups such as oxygen, nitrogen, sulfur, phosphorus, unsaturated bonds and conjugated aromatic rings which serve as adsorption centers¹³. Generally, the tendency to form stronger coordination bonds and, as a result, the inhibition efficiency increases according to the following trend: $O < N < S < P^{14}$.

ONPs are thought to be more advantageous than inorganic and metallic nanoparticles, because of their infinite synthetic routes¹⁵. ONPs are mainly prepared by one of two main methods: emulsification or re-precipitation methods¹⁶. The former is a two-step method; the first step includes the preparation of an emulsification system to create nanodroplets of certain sizes wherein organic compounds were

previously solubilized. The nanoparticles are formed in the second step of the process by numerous mechanisms such as gelation, precipitation, or polymerization¹⁷. The reprecipitation method is of a great interest, it is a one-step method based on the addition of organic material solution into a relatively large volume of another solvent that is poorly miscible with its solution¹⁸. This rapid alteration in the medium persuades the precipitation of organic molecules¹⁹.

The main purpose of this study is the investigation of the inhibition ability of the novel acetohydrazides ONPs towards mild steel corrosion in 1.0 M HCl solution. To the extent of our knowledge, we believe that this is the first report utilizing ONPs as corrosion inhibitors instead of the widely used inorganics. After a through characterization of the freshly prepared ONPs, different techniques were used to monitor their inhibition performance. Techniques such as potentiodynamic polarization (PDP), electrochemical impedance spectroscopy (EIS) complemented by SEM and AFM were used to study the surface morphology of steel alloy after exposure to the HCl solution with and without inhibitors.

2. Experimental part

2.1. Materials and instruments

The corrosion measurements were carried out on Mild steel specimens with a composition in wt.% as follow (C: 0.076, P: 0.012, Mn: 0.192, Si: 0.026, Cr: 0.050, Al: 0.023 and the rest Fe). All chemicals (p-hydroxy benzaldehyde, anhydrous potassium carbonate, ethylchloroacetate, benzaldehyde, hydrazine hydrate, hydrochloric acid, glacial acetic acid) and solvents (ethanol, acetone) were of analytical grade (Sigma - Aldrich) and were used as received without any further purification. TLC was performed using Polygram SIL G/UV 254 TLC plates, and visualization was performed under ultraviolet light at 254 nm and 350 nm. Anhydrous solvents were either supplied by Sigma-Aldrich. ¹H and ¹³C NMR spectra were recorded using a Bruker DPX 400 at 400 MHz and 100 MHz, respectively, and IR spectra were obtained with a Jasco 6300 FTIR. EIMS and FAB-MS spectra were measured using a high-resolution GC-MS (DFS) thermo spectrometer with EI (70 EV). X-ray powder diffraction (XRD) was conducted using D8 Advance diffractometer with a copper target and nickel filter with CuKa radiation (λ = 0.154056 nm). The shape of the nanoparticles was investigated using transmission electron microscopy (TEM) using a Joel JEM 1230 operating at 120 kV. Zeta potential

(ζ) measurements for isoelectric point (IEP) determinations were measured by Zeta sizer Nano ZS (Malvern Instruments Ltd, Malvern, UK). The determined electrophoretic mobilities were converted to ζ -potentials by using Dispersion Technology Software, version 5.03, Malvern Instruments Ltd., UK. Also the surface morphology of the specimens was examined using scanning electron microscope (SEM) using (JSM-6300 JEOL). AFM analysis was carried out using a model VEECO-Nano scope IV multiple AFM/SPM.

2.2. Synthesis of (E)-2-(4-(hydrazonomethyl)phenoxyl) acetohydrazide (H2) nanoparticles



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Scheme 1 Preparation of (E)-2-(4-(hydrazonomethyl)phenoxyl)acetohydrazide

To a stirred solution of p-hydroxybenzaldehyde (1) (0.61 g, 5 mmol) and K₂CO₃ (0.67 g, 5 mmol) in dry acetone (10 mL) the ethyl chloroacetae (0.61 g, 5 mmol) was added dropwise. The reaction mixture was refluxed for 6 h. The solid product was collected by the filtration, washed and recrystallized from ethanol to afford colorless crystals of ester (2). A mixture of ethoxycarbonylmethyl-*p*-oxobenzaldehyde (2) (2.08 g, 0.1 mole), hydrazine hydrate (1.5 g, 0.3 mole) and ethanol (30 ml) was refluxed for 5h. The reaction mixture was cooled to room temperature, collected by filtration and recrystallized from ethanol. Bright yellow powder, yield 1.87 g (90%); mp. 145-147 °C. m/z (EI) = 208.0 [M]⁺ (100%).



Scheme 2 Preparation of *N'(*(E)-benzylidene)-2-(4-((E)hydrazonomethyl) phenoxyl)acetohydrazide

A mixture of **H2** (2.08 g, 0.1 mole), benzaldehyde (1.06 g, 0.1 mole) in ethanol (30 ml) was refluxed for 5h. The reaction mixture was cooled to room temperature, collected by filtration and recrystallized from ethanol. Bright yellow powder, yield 2.67 g (90%); mp. 145-147 °C. m/z (EI) = 296.2 $[M]^+$ (100%).

2.4. Electrochemical measurements

The polarization experiments were carried out in a conventional three-electrode cell with 1 cm² platinum foil as the counter electrode, a saturated calomel electrode as a reference electrode and Mild steel sheet (1 cm x 1 cm) embedded in epoxy resin of polytetrafluoroethylene as the working electrode. Before polarization scanning, working electrode was immersed in the test solution for 30 minute until steady state potential was attained. All potentiodynamic measurements were carried out with a Gamry framework instruments (version 3.20), controlled by a computer which also recorded and stored the data. Measurements were performed in the 1M HCl solution containing different concentrations of the tested ONPs by changing the electrode potential automatically from - 750 to - 200 mV vs. SCE at scan rate of 0.5 mV s⁻¹.

EIS tests were performed at 25 ± 1 °C in a three electrode assembly as above. The EIS spectra were recorded at E_{OC} after immersion of the electrode for 30 minutes in the test solution in the frequency range from 100 kHz and 0.5 Hz and the AC signal was 5 mV peak to peak. A personal computer with EIS300 software and Echem analyst 5.21 was used for data fitting.

3. Results and Discussion

3.1 Characterization of the ONPs

3.1.1 Structural elucidation

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Schemes (1 and 2) displayed preparation of both H2 and H3 nanoparticles. The molecular weights of the synthesized corrosion inhibitors are 208.221 and 296.33 for H2 and H3, respectively, which were calculated based on their proposed molecular formulas (C₉H₁₂N₄O₂) and (C₁₆H₁₆N₄O₂) and confirmed via mass spectrometry measurements. The FT-IR spectra of the ONPs showed absorption bands at 3250 and 3125 cm^{-1} for hydrazide NH-NH₂ and 2819.0 cm⁻¹ for (-CH₂- aliphatic), while carbonyl stretching at 1647 cm⁻¹. The bands at 1510 cm⁻¹ and 1250 cm⁻¹ are for N=C and C-O bonds, respectively. The ¹H-NMR spectrum of H2 shows a singlet at δ 9.39 ppm which is attributed to the NH-NH₂ protons and at δ 4.35 (s, 2H, for -CH₂) and δ 4.47 ppm (brs, 2H, NH₂). While the ¹H-NMR spectrum of H3 exhibits a singlet at δ 9.39 ppm due to the NH-NH₂ protons and at δ 8.03 ppm for phenyl group and δ 5.21 ppm (brs, 2H, NH₂). From ¹³C-NMR for H2 compound, a band at 166.63 ppm due to the carbonyl group, and bands at 115.14, 124.99, 127.24 and 130.25 ppm are from the carbon atoms in the aromatic ring. While ¹³C-NMR for H3 compound, a band appeared at 168.78 ppm for the carbonyl group, and the bands at 114.98, 125.14, 126.80, 127.17, 128.85, 130.25 and 133.79 ppm were from carbon atoms in the aromatic rings.

3.1.2 Morphological and particle size characterization

3.1.2.1 Transmission Electron Microscopy

TEM images for both ONPs are shown in Fig. 1. Both nanoparticles revealed a semispherical shape with a particle size of 3.0 nm and 2.0 nm for H2 and H3 organic

nanoparticles respectively. Furthermore, as shown from the TEM images, the nanoparticles are monodispersed without any notable aggregation.



Figure 1 Transmission electron micrographs for H2 (A) and H3 (B).

3.1.2.2 X-Ray Diffraction (XRD)

XRD patterns of H2 and H3 ONPs showed broad peaks which confirm its presence in the nanoscale as depicted in Fig. 2. Crystallite size measurements were determined from the full-width at half maximum (FWHM) of the strongest peak at $2\theta = 16.3^{\circ}$ and 26.2° for H2 and H3 nanoparticles respectively, using Scherrer's equation $D = K\lambda/(\beta \cos\theta)$. Where, D is the average crystal diameter, β is the full width at half-maximum, K is a constant (K = 0.90), λ is the wavelength (0.154 nm), and θ is the diffraction angle. The determined crystallite sizes were found to be 5.0 nm and 2.3 nm for H2 and H3 nanoparticles respectively.



Figure 2 XRD patterns for H2 and H3 ONPs.

3.1.3 Determination of the Isoelectric Point (IEP)

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The isoelectric point for both H2 and H3 NPs were measured using dynamic light scattering (DLS). The data for H2 NPs exhibited two ionization sites and subsequently two isoelectric points at pH values of 2.3 and 3.6, respectively as shown in Fig. 3A. H2 NPs contained two functionalities: amine group and amide group. The amine is protonated in the acidic medium (HCl), however, its conjugate acid will be uncharged in the strong acidic medium which could explain the zero charge at such an acidic pH value²⁰. On the other hand, the amide group in an acidic medium can undergo hydrolysis and form a carboxyl group which is unprotonated under acidic conditions, thus this could explain the second isoelectric point,²¹ the same can be explained for H3 NPs as shown in Fig. 3B.



Figure 3 Isoelectric point of H2 (A) and H3 (B) ONPs.

3.2 Electrochemical studies

3.2.1 Potentiodynamic polarization study

Tafel curves of bare Mild steel alone and with various concentrations of H2 and H3 NPs were recorded as shown in Fig. 4. The electrochemical parameters including corrosion potential ($E_{corr.}$), corrosion current density ($i_{corr.}$), Tafel cathodic and anodic slopes (β_c , β_a) and efficiency of inhibition (IE%) were obtained from this Figure by extrapolation and the results are presented in Table 1. The values of (IE%) were calculated by the following equation^{22, 23}:

$$IE\% = \frac{i_{Corr.} - i_{Corr.}}{i_{Corr.}} \times 100$$
(1)

where $i_{corr.}$ and $i'_{corr.}$ are the corrosion current in the absence and presence of inhibitors, respectively. The maximum corrosion inhibition efficiencies (IE%) recorded at concentration of 1×10^{-3} M were 88.2 and 96.7% for H2 and H3, respectively. From the results, $i_{corr.}$ was reduced in the presence of the inhibitors especially as their concentrations increased. This was probably due to the inhibitor adsorption on the metallic surface which blocked the active sites on steel surface and protected it from corrosive media^{24, 25}. Depending on the values of $E_{corr.}$, these synthetic ONPs can be classified as cathodic, anodic or mixed-type inhibitors. In the present work, the values of $E_{corr.}$ showed irregular relationship, however, the results listed in Table 1 illustrated that the presence of the inhibitors changed the cathodic and anodic Tafel slopes values

but it was clear that β_c values were greatly affected compared with the values of β_a indicating that the ONPs can be considered as mixed type inhibitors predominately cathodic type inhibitor^{26, 27}. Ultimately affecting both the anodic and cathodic reactions related to metal dissolution and hydrogen evolution, respectively.



Figure 4 Polarization curves for blank Mild-steel in 1M HCl solution and in presence various concentrations of H2 (A) and H3 (B) at 25 °C.

Table 1 Electrochemical data measured using polarization technique for bare mild
steel alloy in 1 M HCl alone and containing various concentrations of H2 and H3
ONPs at 25°C and scan rate 20 mV/min.

	C	i _{corr.,}	-E _{corr.,}	-β _c ,	β _a ,	0	0/ IE	corrosion rate
	Conc., ppm	µA cm ⁻²	mV	mV dec. ⁻¹	mV dec. ⁻¹	Ð	%01E	(CR) mm/year
Blank		3517.0	461.5	304	165			1610.0
	1 x 10 ⁻⁵	1093.0	508.9	230	160	0.689	68.9	500.1
	5 x 10 ⁻⁵	691.0	507.9	210	191	0.804	80.4	316.3
H2	1 x 10 ⁻⁴	498.3	515.6	233	173	0.858	85.8	228.1
	5 x 10 ⁻⁴	444.5	497.8	196	142	0.874	87.4	203.5
	1 x 10 ⁻³	413.5	507.8	207	106	0.882	88.2	189.3
	1 x 10 ⁻⁵	730.2	477.9	287	110	0.792	79.2	331.5
Н3	5 x 10 ⁻⁵	316.6	475.8	199	84	0.910	91.0	168.2
	1 x 10 ⁻⁴	244.3	476.0	189	94	0.931	93.1	140.1
	5 x 10 ⁻⁴	158.1	488.1	219	106	0.955	95.5	122.4
	1 x 10 ⁻³	116.7	485.8	163	88	0.967	96.7	63.7

3.2.2 Electrochemical impedance spectroscopy (EIS)

EIS measures electrochemical changes in situ in which enables monitoring the physical processes occurring at the metal/electrolyte interface^{28, 29}. Fig. 5 shows Nyquist plots recorded for Mild-steel corrosion in the absence and presence of various concentrations of the ONPs inhibitors. The data recorded exhibited a capacitive loop which indicated that the ONPs inhibited the corrosion process by adsorbing at the metal/electrolyte interface^{30, 31}. The addition of ONPs inhibitors to the metal surface resulted in an expansion of the diameter of the semicircles showing a better inhibitive capacity³². The EIS data was fitted using the circuit shown in Fig. 6 which involved R_s (solution resistance of electrolyte), R_{ct} (charge transfer resistance), where R_{ct} refers to the capability of the covering film of the ONPs adsorbed on the metallic surface to hinder the transfer of charges across the metal/solution interface, and CPE (constant phase element) is defined as follows^{33, 34}:

$$Z_{CPE} = \frac{1}{Y_o(jw)^n} \tag{2}$$

where Y_0 is the ratio of the constant phase element, *j* is an imaginary number ($j^2 = -1$), *w* is the angular frequency, n is a deviation parameter related to a phase shift. The values of corrosion inhibitor efficiency for Mild-steel in 1.0 M HCl solution are calculated using the following equation³⁵:

$$IE\% = \frac{R_{ct} - R_{ct.o}}{R_{ct}} x \ 100 \tag{3}$$

where R_{ct} and $R_{ct,o}$ are the resistance of charge transfer for Mild-steel in 1.0 M HCl solution in the presence and absence of the ONPs, respectively. The parameters deduced from the EIS data are displayed in Table 2, they are an accurate examination of the results detected the increase in R_{ct} value with the addition of the ONPs which is assigned to the thin film formed by the inhibitor adsorption on the steel surface^{36, 37}. Also C_{dl} (double layer capacitance) can be calculated as follow³⁸:

$$C_{dl} = Y_o(w_{max})^{n-1} \tag{4}$$

where, w_{max} to refers the frequency at which the imaginary quantum of impedance has acquired the maximum (rad s⁻¹) value. Decreasing the tendency of C_{dl} values with increasing the ONPs concentrations can be elucidated by the Helmholtz type as equation (5)³⁹ which can be attributed to the displacement of water molecules slowly by the ONPs, lowering the local dielectric constant and rustic electrical double layer⁴⁰:

$$C_{dl} = \frac{\varepsilon^o \varepsilon}{d} S \tag{5}$$

where *d* is the electric double-layer thickness, *S* is the surface area of steel electrode, ε *is* the local dielectric constant and ε^{o} is the permittivity of the air. Consequently, the decrease in C_{dl} values lead to constricting the exposed electrode surface area in truculent solution and thus efficiently minimized corrosion of steel⁴¹. Accordingly, the inhibition efficiencies increased with increasing inhibitors concentrations and reached 88.2% for H2 and 96.7% for H3 at 1x10⁻³M. These results of EIS studies were in perfect conformity with the polarization results.



Figure 5 Nyquest plots for corrosion of blank Mild-steel in 1M HCl solution alone and with various concentrations of H2 (A) and H3 (B) at 25 °C.



Figure 6 Circuit model used to fit the EIS Nyquist plots.

Table 2 EIS data of Mild steel corrosion in 1 M HCl with and without various concentrations of H2 and H3 ONPs at 25°C.

	Conc., M	R_s Ωcm^2	$\begin{array}{c} R_{ct} \\ \Omega \ cm^2 \end{array}$	n	C _{dl} μFcm ⁻²	θ	IE%
Blank		1.34	15.4	0.829	105.1		
H2	1 x 10 ⁻⁵	1.25	52.9	0.877	70.4	0.709	70.9
	5 x 10 ⁻⁵	1.13	77.2	0.848	61.2	0.801	80.1
	1 x 10 ⁻⁴	1.08	99.4	0.899	55.3	0.845	84.5
	5 x 10 ⁻⁴	1.46	132.3	0.891	49.7	0.884	88.4
	1 x 10 ⁻³	1.53	156.8	0.901	47.6	0.902	90.2
	1 x 10 ⁻⁵	1.19	77.8	0.834	60.3	0.802	80.2
Н3	5 x 10 ⁻⁵	1.12	225.1	0.858	51.6	0.932	93.2
	1 x 10 ⁻⁴	0.97	272.2	0.846	43.4	0.943	94.3
	5 x 10 ⁻⁴	1.29	322.3	0.876	38.7	0.952	95.2
	1 x 10 ⁻³	1.41	378.2	0.891	34.2	0.959	95.9

3.2.3 Adsorption isotherm

The adsorption of the ONPs on the metallic surface depended on the interactions at the interface between metal and solution where both the adsorbent and adsorbate were present. In this work, the Langmuir adsorption isotherm exhibited the best one that matched with the obtained data and based on the values of the correlation coefficient (R^2) which was almost near to unity. The Langmuir adsorption isotherm can be represented as the following⁴²:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{6}$$

From the previous equation, C is the inhibitor concentration, θ is the coverage area of surface and K_{ads} represents the adsorption-desorption constant. The plots of C/θ against C for the studied ONPs inhibitors at certain temperature are shown in Fig. 7. Gibb's free energy of adsorption (ΔG^o_{ads}) for H2 and H3 were determined using the following equation:

$$\Delta G^{o}_{ads} = -RT \ln \left(55.5 K_{ads}\right) \tag{7}$$

In the above equation, *R* is the gas constant, *T* is the absolute temperature, and 55.5 is the molar concentration of water. The K_{ads} and ΔG^o_{ads} values are given in Table 3 for the investigated ONPs. The type of adsorption of inhibitor molecules on metallic surface can be explained by using the values of ΔG^o_{ads} which is considered one of the most successful techniques for this purpose⁴³. Generally, if the value of ΔG^o_{ads} -20 KJmol⁻¹ or less negative is counted to be physical adsorption which is attributed to electrostatic interaction between the adsorbent and adsorbate⁴⁴, while if the value of ΔG^o is -40 KJ mol⁻¹ or more negative; it is considered to be chemical adsorption which associated with sharing of charge⁴⁵. From the results shown in Table 3, the values of ΔG^o suggested the type of interaction between the ONPs and Mild-steel surface included both physical and chemical adsorption⁴³.



Figure 7 Langmuir adsorption isotherm for corrosion inhibition of Mild-steel in 1M HCl solution in presence of H2 and H3 ONPs.

Table 3 Equilibrium constant (K), free energy of binding (ΔG_{ads}) of H2 and H3 for corrosion of Mild steel in 1 M HCl at 25°C

Inhibitor	Langmuir isotherm				
	\mathbb{R}^2	K (M ⁻¹)	- $\Delta G_{ads} (kJ mol^{-1})$		
H2	0.99998	2.2×10^5	40.4		
H3	0.99997	2.6×10^5	42.2		

3.3 Characterization of steel surface

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3.3.1 Scanning Electron Microscopy analysis

SEM micrographs of steel samples after the exposure to 1 M HCl solution for 24 h in the absence and presence of the optimal concentration of the ONPs $(1x10^{-3}M)$ are depicted in Fig. 8 (A-C). From these micrographs, it was obvious that the steel surface subjected to the blank solution (Fig. 8 A) appeared porous and rough with random scratches due to loss in the resistance against corrosion in the aggressive media. However, the addition of the inhibitor ONPs to the acidic media protected the steel surface from corrosion and a smooth surface was observed Fig. 8 (B, C). The

smoother surface was more pronounced in the presence of H3 compared with H2. Thus, it can be concluded that the presence of H3 and H2 ONPs decreased the aggressive attack of the acidic solution, confirmed by the high efficiency of the protective film formed by the ONPs on the surface of mild steel.

3.3.2 Atomic force microscopy analysis

AFM is considered an important tool in studying the morphology of surfaces which helps in explaining the corrosion process at the interface between metal and solution at the nanoscale and microscale. The three-dimensional AFM graphs of mild-steel surface in 1 M HCl solution with and without the studied compounds H3 and H2 (1 x 10^{-3} M) are depicted in Fig. 8 (A-C). Clearly, the AFM pattern of steel surface exposed to 1 M HCl solution displayed a very porous surface with large and deep random pores as a result of the aggressive media exposure (Fig. 8 A). On the other hand, in the presence of the ONPs, relatively smooth and flat surfaces were obtained as shown in Fig. 8 (B, C). These findings confirmed that the dissolution rate of steel was decreased and controlled. The smoother surface obtained can be attributed to the protective thin film formed by adsorption of ONPs on the steel surface.



Figure 8 SEM and AFM micrographs of Mild steel surface after immersion in 1M HCl solution without (A) and with the optimum concentration of H2 (B) and H3 (C) at 25 $^{\circ}$ C, scale bare in SEM is 10 μ m.

3.4. Suggested corrosion inhibition mechanism

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It is essential to postulate the corrosion inhibition mechanism of the studied new organic nanoparticles to steel surface in the acidic medium. According to the literature, it is well known that the organic compounds can suppress or prevent metals dissolution by the physical or chemical adsorption on their surfaces⁴⁶. In the present work the adsorption of the investigated ONPs was confirmed to be a physisorption process due to the electrostatic interaction at the metal/solution interface based on the Langmuir isotherm. Several factors are responsible for the adsorption of the inhibitors on the metal surface such as the presence of unshared electron pairs on oxygen and nitrogen atoms and/or the π -electrons of the aromatic rings which can form a donor/acceptor surface complex with the vacant d-orbitals of the surface metal⁴⁷.

The adsorption of the investigated ONPs can be proved depending on the surface coverage results (θ) which increased with increasing the inhibitors concentration as shown in Table 1; this confirmed their effective protection of the steel surface from HCl attacking. In aqueous acidic solutions, the H2 and H3 existed either as neutral or positively charged particles as confirmed by the isoelectric point studies. However, as previously reported that the steel surface bears a positive charge in an acidic media⁴⁸, so it is difficult for these molecules to interact with the positively charged steel surface because of the electrostatic repulsion. Interpretation of this problem depended on the presence of the negatively chloride ions with the smaller degree of hydration which is responsible on the presence of excess of negative charges which acted as a mediator between the adsorbed inhibitor molecules and metal surface.

Furthermore, the H3 compound showed higher inhibition efficiency compared with H2 compound due to its higher molecular weight and the presence of one additional aromatic ring which resulted in better stacking on the metal surface and hence increased the protection from corrosion. The layer formed on the steel surface is believed to suppress both the anodic and cathodic reactions on the steel surface as demonstrated from Tafel slope. One of the important findings in this study is the pronouncedly high inhibition efficiency which could be a result to the presence of the nanoparticles that have high surface area which was responsible for blocking the active sites on the steel surface making it withstand the dissolution in the aggressive environments.

4. Conclusion

New ONPs of acetohydrazides were successfully synthesized by re-precipitation method. Structural elucidation, morphological and particle size characterizations were performed to confirm the structure, spherical and nanoscale particle size of both nanoparticles. Subsequently, the synthesized ONPs were effectively used as corrosion inhibitors for mild steel in acidic medium. The study showed that the investigated ONPs can efficiently suppress the mild steel dissolution in 1 M HCl solution. Polarization results confirmed controlled the anodic and cathodic reactions in the presence of ONPs. Superior inhibition efficiencies of 88.2% and 96.7% were obtained using small concentration $(1 \times 10^{-3} \text{ M})$ of H2 and H3, respectively. The inhibition mechanism occurred through the adsorption of the ONPs on the metallic surface blocking its active sites, which was confirmed by SEM, AFM and impedance results. The values of the adsorption energy obtained supported the physical adsorption of these molecules which further validated the results. The outstanding results obtained may help in the opportunity for applying the investigated ONPs in the industrial applications and these ONPs could be further chemically modified to obtain particles of different chemical nature suitable for various applications.

References

- 1. U. Eduok, E. Jossou, A. Tiamiyu, J. Omale and J. Szpunar, *Industrial & Engineering Chemistry Research*, 2017, 56, 5586-5597.
- J. Aljourani, K. Raeissi and M. A. Golozar, *Corrosion Science*, 2009, **51**, 1836-1843.
- M. Chellouli, D. Chebabe, A. Dermaj, H. Erramli, N. Bettach, N. Hajjaji, M. P. Casaletto, C. Cirrincione, A. Privitera and A. Srhiri, *Electrochimica Acta*, 2016, 204, 50-59.
- X. Zheng, S. Zhang, W. Li, M. Gong and L. Yin, *Corrosion Science*, 2015, 95, 168-179.
- 5. L. Hu, S. Zhang, W. Li and B. Hou, Corrosion Science, 2010, 52, 2891-2896.
- G. Wang, S. Liu, S. Wei, Y. Liu, J. Lian and Q. Jiang, Scientific Reports, 2016, 6, 20933.
- 7. A. Fateh, M. Aliofkhazraei and A. R. Rezvanian, *Arabian Journal of Chemistry*, 2017.
- 8. A. S. Fouda, M. A. Ismail, A. S. Abousalem and G. Y. Elewady, *RSC Advances*, 2017, 7, 46414-46430.
- 9. M. A. Migahed and I. F. Nassar, *Electrochimica Acta*, 2008, 53, 2877-2882.
- 10. C. Verma, M. A. Quraishi, K. Kluza, M. Makowska-Janusik, L. O. Olasunkanmi and E. E. Ebenso, *Scientific Reports*, 2017, 7, 44432.
- 11. E. E. Oguzie, Pigment & Resin Technology, 2005, 34, 321-326.
- A. A. Al-Amiery, A. A. Kadhum, M. A. H. Alobaidy, B. A. Mohamad and S. P. Hoon, *Materials*, 2014, 7.
- M. Yadav, R. R. Sinha, S. Kumar, I. Bahadur and E. E. Ebenso, *Journal of Molecular Liquids*, 2015, 208, 322-332.
- 14. K. Xhanari and M. Finšgar, Arabian Journal of Chemistry, 2016.
- 15. L. Kang, Z. Wang, Z. Cao, Y. Ma, H. Fu and J. Yao, *Journal of the American Chemical Society*, 2007, **129**, 7305-7312.
- 16. S. Krishnakumar and K. R. Gopidas, *Journal of Materials Chemistry B*, 2014, **2**, 5576-5584.
- 17. J. P. Rao and K. E. Geckeler, Progress in Polymer Science, 2011, 36, 887-913.
- 18. A. J. Gesquiere, T. Uwada, T. Asahi, H. Masuhara and P. F. Barbara, *Nano Letters*, 2005, 5, 1321-1325.
- 19. A. Y. Utekhina and B. S. Gleb, Russian Chemical Reviews, 2011, 80, 219.
- 20. S. H. Hilal, S. W. Karickhoff and L. A. Carreira, *Talanta*, 1999, 50, 827-840.
- 21. D. Zahn, European Journal of Organic Chemistry, 2004, 2004, 4020-4023.
- 22. A. Abdel Nazeer, N. K. Allam, G. I. Youssef and E. A. Ashour, *Industrial & Engineering Chemistry Research*, 2011, **50**, 8796-8802.
- 23. A. A. Nazeer, N. K. Allam, A. S. Fouda and E. A. Ashour, *Materials Chemistry* and *Physics*, 2012, **136**, 1-9.
- 24. R. Yıldız, T. Doğan and İ. Dehri, Corrosion Science, 2014, 85, 215-221.
- Y. Qiang, L. Guo, S. Zhang, W. Li, S. Yu and J. Tan, *Scientific Reports*, 2016, 6, 33305.
- 26. M. A. Chidiebere, E. E. Oguzie, L. Liu, Y. Li and F. Wang, *Journal of Industrial* and Engineering Chemistry, 2015, 26, 182-192.
- 27. L. R. Chauhan and G. Gunasekaran, Corrosion Science, 2007, 49, 1143-1161.
- A. Abdel Nazeer, H. M. El-Abbasy and A. S. Fouda, *Research on Chemical Intermediates*, 2013, 39, 921-939.
- 29. C. B. Verma, M. A. Quraishi and A. Singh, *Journal of the Taiwan Institute of Chemical Engineers*, 2015, **49**, 229-239.

- 30. A. Abdel Nazeer, H. M. El-Abbasy and A. S. Fouda, *Journal of Materials Engineering and Performance*, 2013, **22**, 2314-2322.
- M. Chevalier, F. Robert, N. Amusant, M. Traisnel, C. Roos and M. Lebrini, *Electrochimica Acta*, 2014, 131, 96-105.
- Q. Deng, H.-W. Shi, N.-N. Ding, B.-Q. Chen, X.-P. He, G. Liu, Y. Tang, Y.-T. Long and G.-R. Chen, *Corrosion Science*, 2012, 57, 220-227.
- 33. D. Daoud, T. Douadi, H. Hamani, S. Chafaa and M. Al-Noaimi, *Corrosion Science*, 2015, **94**, 21-37.
- M. BinSabt, A. A. Nazeer, M. Madkour and F. Al-Sagheer, *RSC Advances*, 2016, 6, 6888-6895.
- 35. F. Zhang, J. Pan and P. M. Claesson, *Electrochimica Acta*, 2011, 56, 1636-1645.
- C. Verma, A. Singh, G. Pallikonda, M. Chakravarty, M. A. Quraishi, I. Bahadur and E. E. Ebenso, *Journal of Molecular Liquids*, 2015, 209, 306-319.
- C. Verma, M. A. Quraishi, E. E. Ebenso, I. B. Obot and A. El Assyry, *Journal of Molecular Liquids*, 2016, 219, 647-660.
- M. A. Hegazy, A. A. Nazeer and K. Shalabi, *Journal of Molecular Liquids*, 2015, 209, 419-427.
- A. Biswas, S. Pal and G. Udayabhanu, *Applied Surface Science*, 2015, 353, 173-183.
- E. McCafferty and N. Hackerman, *Journal of The Electrochemical Society*, 1972, 119, 146-154.
- 41. I. B. Obot and A. Madhankumar, *Journal of Industrial and Engineering Chemistry*, 2015, 25, 105-111.
- 42. R. Karthikaiselvi and S. Subhashini, *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 2014, **16**, 74-82.
- 43. L. O. Olasunkanmi, M. M. Kabanda and E. E. Ebenso, *Physica E: Low*dimensional Systems and Nanostructures, 2016, **76**, 109-126.
- C. M. Goulart, A. Esteves-Souza, C. A. Martinez-Huitle, C. J. F. Rodrigues, M. A. M. Maciel and A. Echevarria, *Corrosion Science*, 2013, 67, 281-291.
- 45. M. A. Amin and M. M. Ibrahim, Corrosion Science, 2011, 53, 873-885.
- A. A. Nazeer, E. A. Ashour and N. K. Allam, *Materials Chemistry and Physics*, 2014, 144, 55-65.
- 47. N. A. F. Al-Rawashdeh and A. K. Maayta, *Anti-Corrosion Methods and Materials*, 2005, **52**, 160-166.
- 48. X. Wang, H. Yang and F. Wang, Corrosion Science, 2011, 53, 113-121.

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