Egyptian Journal of Chemistry

Pyridinium Bromide Derivatives as Corrosion Inhibitors For Mild Steel in 1M H$_2$SO$_4$

Mohammad Mouayad,[a*] Mehdi Salih Shihab[a]

[a]Department of Chemistry, College of Science, Al-Nahrain University, Baghdad, Iraq

Abstract

In this work, we present a study on the synthesis and characterization of a new series of pyridinium salts, namely 4-(2-((1E,2E)-3-phenylallylidene)hydrazine-1-carbothioamido)-1-propylpyridin-1-ium bromide, P1; (E)-3-(2-(4-(dimethylamino)benzylidene)hydrazine-1-carbothioamido)-1-ethylpyridin-1-ium bromide, P2; (E)-3-(2-(4-(dimethylamino)benzylidene)hydrazine-1-carbothioamido)-1-propylpyridin-1-ium bromide, P3; using spectroscopic techniques such as IR and ^{1}H NMR, as well as the evaluation of their ability to inhibit mild steel corrosion in 1 M H$_2$SO$_4$ at 20 °C using weight loss techniques and scanning electron microscopy. The investigation yielded that the Schiff bases and Pyridinium salts derivatives were successfully synthesized as suggested by the characterization results. In 1 M H$_2$SO$_4$ solution, Pyridinium salts derivatives showed substantial inhibitive activities for mild steel corrosion. Their inhibition efficiencies increased with increasing concentration of inhibitors. The adsorption of the studied compounds on the surface of mild steel follows the Langmuir isotherm model.

Keywords: Corrosion inhibition, Pyridinium salt, mild steel, H$_2$SO$_4$, weight loss measurements, scanning electron microscopy

Introduction

The increasing use of acidic solution in metal cleaning processes, as well as the consequent metal corrosion, has presented researchers in materials engineering with difficult issues in terms of meeting environmental standards and industrial units [1]. When compared to other alloys, mild steel's appeal in industrial applications is due to its high mechanical strength, availability, and low cost. Steels, on the other hand, are extremely prone to corrosion in ordinary aqueous conditions, and the rate of corrosion is especially high at acidic pHs. [2, 3].

The growing inclination of metals to remain in their natural state of oxides, as opposed to the highly energetic pure metallic form, is the driving force for corrosion. Metal corrosion in mineral acids is a huge loss of resources and money. Corrosion inhibitors have been used to combat aqueous and process industrial corrosion. The structural capabilities of inhibitors, as well as their unique interaction with corrosion active centers on the metal surface, prompted the creation of novel inhibitors by

the scientific community. Organic compounds having heteroatoms [4–6], the attendance of aromatic rings and multiple bonds [7, 8] may efficiently shield metal surfaces from corrosive environment by forming a protective layer on the metal surface. [9, 10]. The protective capability of these compounds is frequently due to their chemical adsorption or physical adsorption (or mix adsorption) on the metallic interface. [11].

The shape of the aromatic and aliphatic moieties of the inhibitor molecule, as well as concentration, pH, nature of the acid anion, nature of the metal, chemical substituents and functional groups present, can all affect the inhibitor's adsorption mechanism. [12].

In general, the adsorption depends on (i)the nature and the state of the metal surface, (ii) the type of corrosive environment and (iii) the chemical structure of inhibitor [13,14]. The pyridine skeleton is a component of numerous natural compounds, including vitamins, coenzymes, and alkaloids. It is utilized as a solvent and reagent in industrial

chemistry [15]. Pyridine moiety plays an active role in the design of many pharmaceutically active compounds with its specific basic structure, water solubility, stability, and the ability to make hydrogen bond [16].

Some authors have explained that not only the p electron of the Schiff bases enter unoccupied orbitals of transition metals, but the π* orbital can also accept the electrons of transition metal d-orbitals to form feedback bonds [17] and thereby enabling existence in metal-inhibitor bond. Schiff bases have been recently reported as effective corrosion inhibitors for steel, aluminum and copper in acidic media. The greatest advantages of Schiff bases are [18, 19]:

(a) They can be synthesized conveniently from inexpensive raw materials

(b) They contain the electron cloud on the aromatic ring or, the electronegative atoms such as nitrogen and sulfur in the relatively long chain compounds

(c) Harmless for environment, which encouraged us totest this type of inhibitor.

They have the general formula R'0-C=N-R″ where R' and R″ are alkyl, aryl, cycloalkyl or heterocyclic groups and are the product of the condensation process between an amine and a ketone (or an aldehyde) [20].

The present work intends to investigate the function of 14-(2-((1E,2E)-3-phenylallylidene)hydrazine-1-carbothioamido)-1-propylpyridin-1-ium bromide, P1; (E)-3-(2-(4-(dimethylamino)benzylidene)hydrazine-1-carbothioamido)-1-ethylpyridin-1-ium bromide, P2; (E)-3-(2-(4-(dimethylamino) benzylidene) hydrazine-1-carbothioamido)-1-propylpyridin-1-ium bromide, P3; (figure1) as an inhibitor to mitigate mild steel corrosion in sulfuric acid by weight loss and using scanning electron microscopy to investigated the morphological of mild steel surface in 1 M H2SO4 solution without and with prepared pyridinium salt (P1, P2, and P3) for 24 hours at 20° C.

2. Experimental

2.1 Materials

The following chemicals were utilized straight from their specified suppliers, without additional purification:

(3-amino pyridine/ Aldrich/ 99%), (Carbon disulfide /Alpha /99%) ,(Sodium bicarbonate / BDH/ 99%) ,(Dimethylformamide / Aldrich /99.8%),(

Cobalt(II) chloride hexahydrate / Thomas Baker /99%) ,(Ammonia / BDH/ 99%),(Ethanol/ Honeywell /99%),(Hydrazine hydrate/ BDH /85%) ,(Diethyl ether/ Thomas Baker /98%),(Sulfuric acid / CDH /98%) ,(Glacial acetic acid/ Merk /99%) ,(Cinnamaldehyde/ Merk /99%),(4-dimethyl amino benzaldehyde / BDH/ 99%),(2-thiophen carboxaldehyde /Merk /99%) ,(4-Nitro benzaldehyde /Geekee bio /97%),(4-Chloro benzaldehyde/ Thomas baker /98%),(Ethyl bromide / Merk /99%),(Propyl bromide /Merk /99%),(Butyl bromide / BDH /99%). Mild steel samples (composition in weight: 0.22% C, 0.31% Si, 0.60% Mn, 0.04% P, 0.06% S and the remainder Fe)
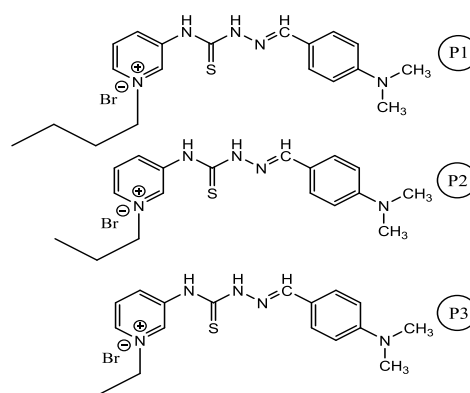

Figure1. The molecular formula of the proposed inhibitors (P1, P2 and P3)

2.2 Instrumentation

The infra-red spectra of the synthesis compounds were recorded using buker (ALPHA) FTIR spectrometer in the transmission range of $(4000-400)cm^{-1}$, AL-Nahrain University. ^{1}H-NMR spectra were recorded on nuclear magnetic resonance Bruker spectrophotometer model Ultrasheild 400 MHz using tetramethylsilane internal standard and DMSO-d6 as solvent (Isfahan University of Technology (IUT), Iran). Melting point was determined by the open capillary method using Gallenkamp melting point apparatus, ALNahrain University, Department of Chemistry. And Balance, Ohaus, PA 114, USA.

2.3. Synthesis of pyridinium salts:

Pyridinium bromide derivatives corrosion inhibitors, namely: 4-(2-((1E,2E)-3-phenylallylidene)hydrazine-1-carbothioamido)-1-propylpyridin-1-ium bromide, P1; (E)-3-(2-(4-

(dimethylamino)benzylidene)hydrazine-1-carbothioamido)-1-ethylpyridin-1-ium bromide, P2; (E)-3-(2-(4-(dimethylamino)benzylidene)hydrazine-1-carbothioamido)-1-propylpyridin-1-ium bromide, P3; were synthesized as follow:

2.3.1 Synthesis of 1-(pyridin-3-yl) thiourea (A1)

In a Round bottom flask, fitted with magnetic stirrer, a reflux condenser was placed (1.88g, 0.02 mol) of 3-amino Pyridine, (10 eq, and 0.2 mol) of carbon disulfide, and (3.36 g, 0.04 mol, 2 eq) of Sodium bicarbonate with 12 mL DMF. The stirrer was started after the addition is complete, the mixture was heated with continuous stirring for 2 hour; then the (2.81 g, 25 mol %) of the Cobalt (II) sulfate was added and continuous stirring for 2hs. then (2 mL) of ammonia solution was added with continuous stirring for 1 h. After that, the precipitate was filtered and dried to obtain the product [21,22], (see **scheme 1**).

2.3.2. Preparation of N-(pyridin-3-yl) hydrazinecarbothioamide (A2)

1-(pyridin-3-yl) thiourea (A1) (1.53 g) dissolved in (30 mL) of absolute ethanol, (2.5 mL) hydrazine hydrate added fraction wise. Mixture was refluxed for (10-12 hs) with stirring. The content concentrates to half of its volume and poured onto crushed ice. The resultant precipitate was filtered. Dried and recrystallized from ethanol [23], (see Table 1, scheme 1).

2.3.3. Synthesis of Schiff base (A3):

To (20 mL) hot ethanol (R3 0.02 mol) and reactant (4-Dimethylaminobenzaldehyde, 0.02 mol) were dissolved and to this mixture some drop of glacial acetic acid was added. The reaction mixture was then refluxed on a water bath for (8 hs). The mixture was allowed to stand for (24 hs) at room temperature. The product was collected and recrystallized with ethanol-chloroform mixture, (see Table 1, scheme 1). [24,25]

2.3.4. Synthesis of Pyridinium salts (P1, P2, and P3):

A mixture of (0.01 mol) a Schiff base product (A3) and (0.01 mol) of a proper alkyl halide (Bromoethane, 1-Bromopropane, 1-Bromobutane) in 10 mL of ethanol was allowed to stand overnight at room temperature. The mixture was then heated at
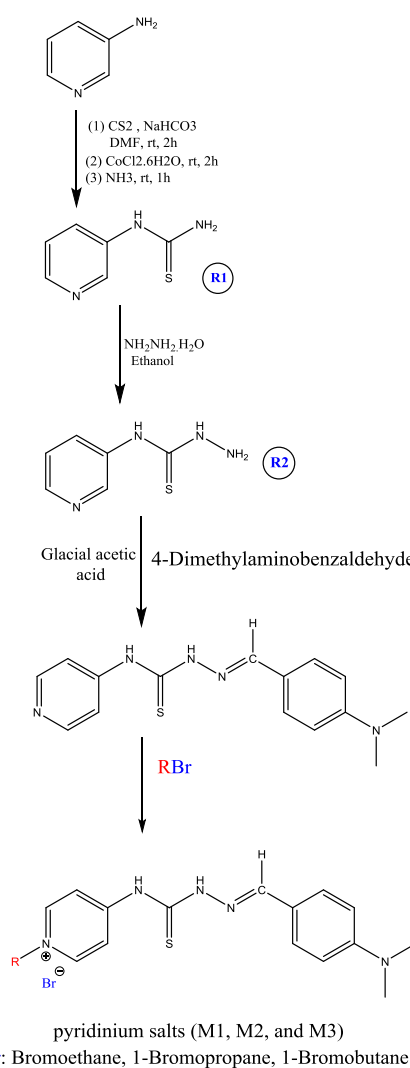
the reflux temperature for 24 hours. Then the product was filtered, washed with ethanol and dried, (see Table 1, scheme1). [26]

2.4 Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using Scanning Electron Microscope (FEI_ Company, Netherlands, Inspect S50 (Model) with an accelerating voltage of 30 kV.

3. Results and Discussion

The pyridinium bromide derivatives (P1, P2, and P3) used in this study is synthesized according to Scheme 1.

pyridinium salts (M1, M2, and M3)
RBr: Bromoethane, 1-Bromopropane, 1-Bromobutane

Scheme 1: The pyridinium salts' synthesis process (P1, P2, and P3).

The procedures listed above were used to make pyridinium bromide derivatives (P1, P2, and P3). The FTIR spectral data and physical characteristics of the

prepared compounds are summarized in Table 1, although the ^{1}H-NMR spectral data in ppm for the compounds (M1, M2, and M3) are included in Table 2, see Figure 2, 3, and 4.

Table 1: Physical characteristics of new produced compounds

Comp. No.	Chemical formula	M.W. (g/mol)	Color	M.P. ºC	Yield %	Comp. No.
A1	$C_6H_7N_3S$	153.20	Brown	Decomp.	96	A1
A2	$C_6H_8N_4S$	168.22	Light Gray	Decomp.	85	A2
A3	$C_{15}H_{17}N_5S$	299.40	Yellow green	261	90	A3
P1	$C_{18}H_{21}BrN_4S$	405.36	Dark red	258	74	P1
P2	$C_{18}H_{24}BrN_5S$	408.36	Goldenrod	228	68	P2
P3	$C_{17}H_{22}BrN_5S$	422.39	Saddle brown	227	69	P3

Table 2. FTIR spectral data for compounds (A1, A2, A3, P1, P2, and P3) in cm^{-1}.

Comp. No.	v N-H	v C-H aromatic	v C=N	v C=C	v C=S	v C-N
A1	3525	3110	1654	1485	1419	1111
A2	3520, 3400	3197	1651	1546	1481	1014
A3	3429	3172	1637	1600	1413	1174
P1	3403	3180	1647	1520	1426	1166
P2	3410, 3475	3168	1691	1517	1423	1171
P3	3410	3132	1596	1516	1431	1172

Comp. No.	Compound structure	1H-NMR data of (δ-H) in ppm
P1		1H of N-H (pyridine-ring -NH- moiety) (9.6); 1H of NH (-NH-N=CH-) (8.7); 1H of N=CH- (8.5); 4H of pyridine-ring (7.7-8.5); 4H of phenyl- rings (6.7-7.8);6H of two CH3 group (-N(CH3)2) (3.0); 2H of –N+-CH2 group (3.6); 7H of aliphatic chain (0.8-3.2)
P2		1H of N-H (pyridine-ring -NH- moiety) (9.6); 1H of NH (-NH-N=CH-) (8.6); 1H of N=CH- (8.4); 4H of pyridine-ring (7.6-8.5); 4H of phenyl- rings (6.7-7.6);6H of two CH3 group (-N(CH3)2) (2.9); 2H of –N+-CH2 group (3.7); 5H of aliphatic chain (0.8-3.0)
P3		1H of N-H (pyridine-ring -NH- moiety) (9.6); 1H of NH (-NH-N=CH-) (8.8); 1H of N=CH- (8.4); 4H of pyridine-ring (7.6-7.9); 4H of phenyl- rings (6.7-7.7);6H of two CH3 group (-N(CH3)2) (2.9); 2H of –N+-CH2 group (4.1); 5H of CH3 group (0.8-2.2)

Table 3. The ^{1}H-NMR spectral data of compounds (P1, P2, and P3) in ppm

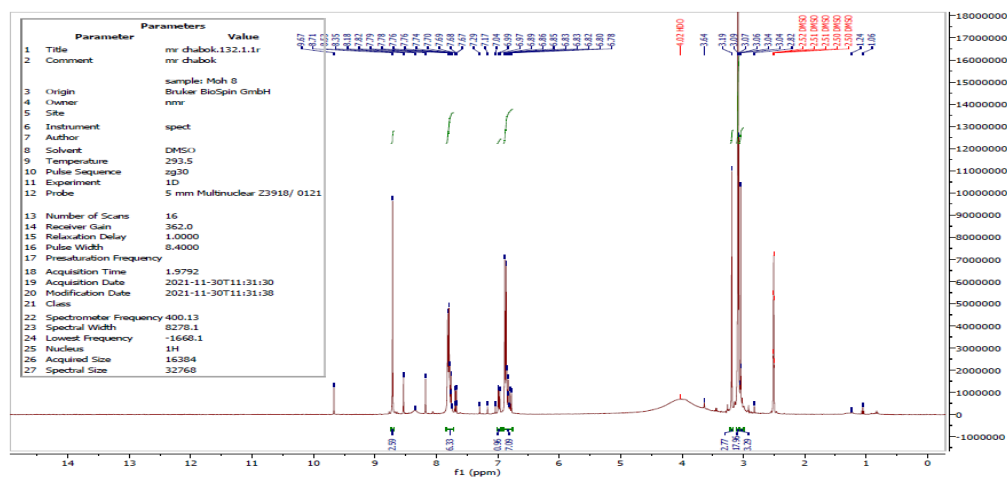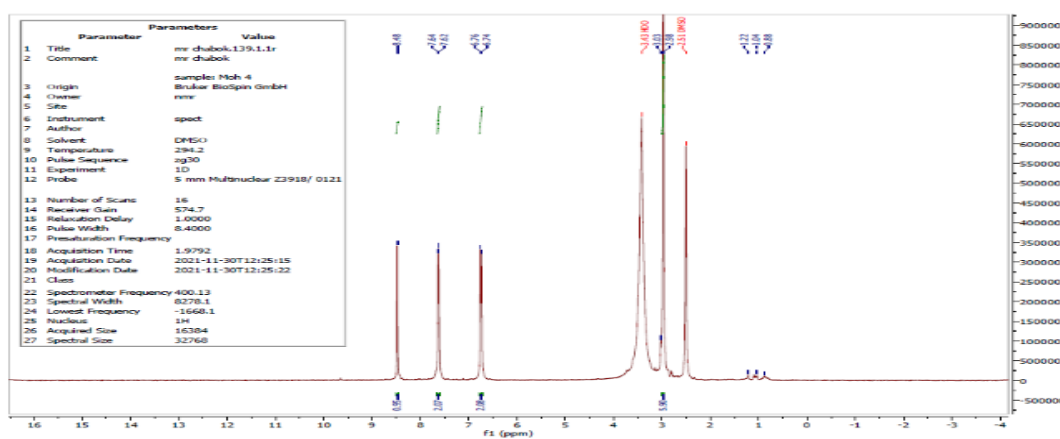**Figure 2.** ^{1}H-NMR of compound (P1)

Figure 3. ^{1}H-NMR of compound (P2)

3.2 Gravimetric method:

In this part of the study, we carried out weight loss measurements on mild steel in 1 M H_2SO_4 solution in the absence and in the presence of different concentrations (0.0005, 0.001, 0.005and 0.01) M of inhibitors (P1,P2, and P3) for 24 hrs.

The weight loss test is most straightforward, productive in relative to its cost, and widely used method for determining corrosion inhibition efficiency. Typically, the initial step is to chop the metallic sample specimen in inquiry into small pieces. Known-diameter forms, which are then degreased, cleaned, and polished. Following that, the samples are submerged in the corrosive medium for certain duration of time, 24 hours, and then cleaned according to ASTM standard protocols [26-29].

Emery papers were used to polish the disc forms of 300, 500, 700, 1000 grits till a clean Mild Steel surface is achieved. To reveal the polish surfaces, it was extensively washed with distill water and Acetone micro structure; Remove any polish residues as well as any greases that may have accumulated. Firstly, Mild Steel specimen was weighted in a digital Balance. Then after, the samples were suspend in a 250 milliliter Beaker contained an acid solution (1 molar H_2SO_4) and thoroughly submerged in it with and without inhibitors in different concentration (0.0005, 0.001, 0.005and 0.01) M for 24 h. at 25° C. After a 24 h. exposure period, the samples were removed, rinsed with water to eliminate any corrosive product, and then cleaned by Acetone. Then Dried and reweighed. The average W.L. is calculated by different in weight between before and after immersions [30].

The corrosion rate (C_R) is defined as the pace at which a material deteriorates in a specific

environment. It's also known as the amount of corrosion loss per year in thickness. The (C_R; mg cm^{-2} h^{-1}) is calculated using the following relationship:

$$C_R = \frac{w}{At} \tag{2.1}$$

Where w symbolizes the average weight loss (mg), A denotes the area of the sample (cm^2), and t denotes the time of exposure (h). The surface coverage (θ) and the corrosion inhibition efficiency ($\eta\%$) can be determined from the values of the C_R [31-34]:

$$\theta = \frac{C_R - C_{R(i)}}{C_R} \tag{2.2}$$

$$\eta\% = \frac{C_R - C_{R(i)}}{C_R} \times 100 \tag{2.3}$$

Where C_R and $C_{R(i)}$ denote the corrosion rates obtained in the absence and presence of a corrosion inhibitor correspondingly. Alternatively, the C_R can be expressed into its standard unit (mm y^{-1} or mmpy) using the following relationship [36,37]:

$$C_R = \frac{87.6w}{Atd} \tag{2.4}$$

Where d represents the density of the metal sample in mg cm^{-3}

After 24 hours of immersion at 20° C, the corrosion rate and inhibition efficiency obtained from weight loss measurements at different concentrations of the suggested inhibitors (P1, P2, and P3) are presented in Table 3 and depicted in Figures 2 and 3.

Table 4: Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption for mild steel in 1 M H$_2$SO$_4$ by using weight loss measurements.

Concentration (M)	Corrosion rate (mg.cm^{-2}.h^{-1})	E%	θ	ΔG°ads (kJ. mol^{-1})
Blank	4.1995			
P1				
5×10^{-4}	1.1367	72.93	0.7293	
1×10^{-3}	0.4594	89.06	0.8906	-31.05
5×10^{-3}	0.0429	98.97	0.9897	
1×10^{-2}	0.0120	99.71	0.9971	(R² = 0,9999)
P2				
5×10^{-4}	0.9132	78.25	0.7825	
1×10^{-3}	0.4576	89.10	0.8910	-31.41
5×10^{-3}	0.0481	98.85	0.9885	
1×10^{-2}	0.0084	99.79	0.9979	(R² = 0,9999)
P3				
5×10^{-4}	1.1754	72.01	0.7201	
1×10^{-3}	0.5640	86.56	0.8656	-30.71
5×10^{-3}	0.1445	96.55	0.9655	
1×10^{-2}	0.0624	98.51	0.9851	(R² = 0,9999)

Corrosion rate and inhibitor efficiency were measured using different inhibitor concentration are presented in Table 3-5. These results point to the importance of Adsorption and surfaces Coverage in corrosion inhibition, with increase as inhibitor concentration increases. The amount of molecular adsorbed on the metallic surfaces at optimum concentration increase as the inhibitor concentration rises, yielding in more active portions of the metallic being shielded by the inhibitory molecule. This indicates that inhibitor molecules adsorption on the mild steel surface, resulting in the creation of a surface protective coating that lowers active sites on the metal surface and so improves corrosion resistance [38-42].
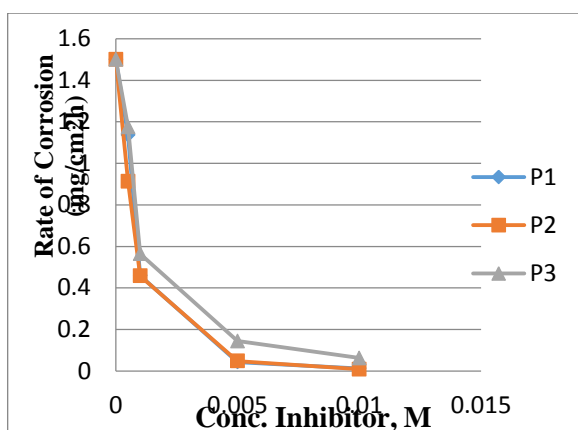
Figure 4. Effect of inhibitor concentrations on the inhibition efficiency for mild steel 1M H2SO4 at 20°C for suggested inhibitors (**P1-P3**)

Figure 5. Effect of inhibitor concentrations on the rate of corrosion for mild steel 1M H2SO4 at 20°C for suggested inhibitors (**P1-P3**).

The inhibitor molecule works through adsorption, which follows the Langmuir adsorption isotherm, to block active sites on metal surfaces. In Figure 3-68, we represent the calculated isotherm for the studied pyridinium salt (P1, P2, and P3). These isotherms illustrate that organic molecule adsorption on metal surfaces is monolayer [43-45].
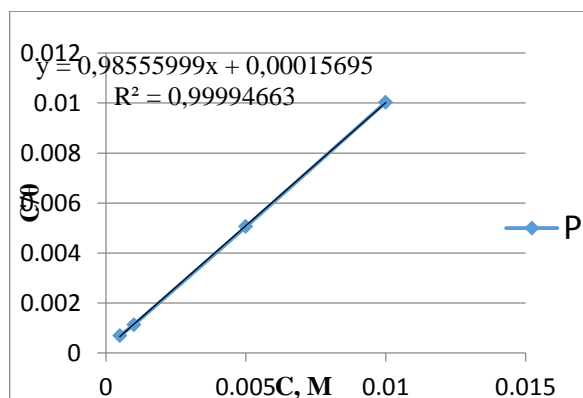

Figure 6. Langmuir adsorption of (P1) of the mild steel surface in 1 M H₂SO₄ solution.

Values of adsorption energy ΔG° ads, which are presented in Table 3-5, may also be obtained using the Langmuir isotherm. From Table 3-5 the ΔG° ads values for the studied inhibitors the adsorption for pyridinium salts (P1,P2, and P3).

The Adsorption of Pyridinium salt (P1,P2, and P3) is determined by the (gibbs free energy adsorption) values for the investigated inhibitor Mild Steel surfaces in 1 molar sulfuric acid a combination chemisorption and physisorption (comprehensive adsorption) [46,48] .
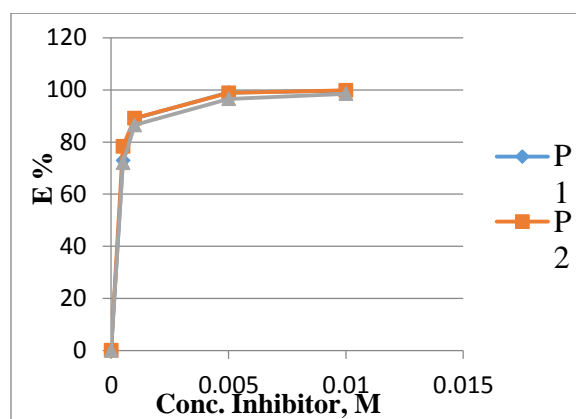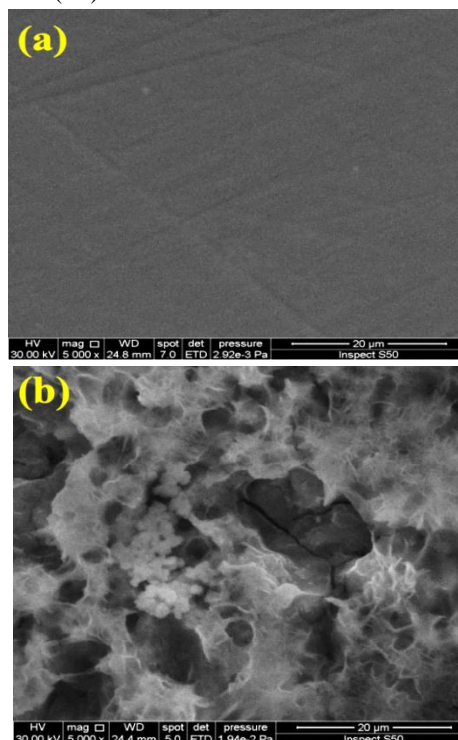
3.2. Scanning electron microscopy (SEM)

Figure 7 shows SEM images for Mild Steel samples immersed, for 24 h, in 1 M H₂SO₄ solution in absences of inhibitor the (figure 7a), after retrieving from 24h Immersion in 1 molar sulfuric acid solutions without inhibitory (figure 7 b), and with inhibitor (figure 7c). SEM could examine the morphological structure as well as the influence of the inhibitor on the sample's corrosion. As shown samples immersed in acid solution (1M H2SO4) containing inhibitor (figure 7c) is smoother compared with the one immersed in H2SO4 solution (figure 7b), revealing the inhibition of corrosion of steel by inhibitor (P1).
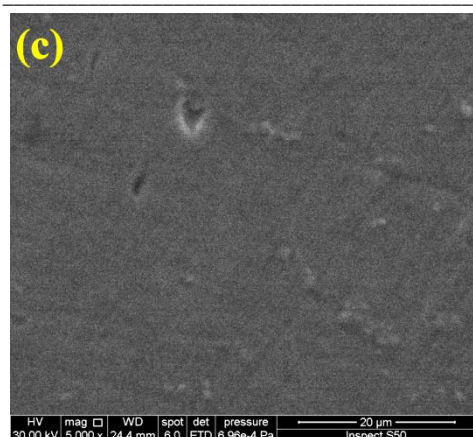
Figure 7: SEM micrographic of Mild Steel surfaces (A) polished steel sample; before immersion (b) After retrieving from 24h Immersion in 1 molar sulfuric acid solutions without inhibitory, (c) with inhibitor (P1)

4. Conclusion

Pyridinium salts derivatives have been synthesized and characterized using FTIR and ^{1}HNMR as well as melting point. Gravimetric analysis and scanning electron microscopy was used to study the inhibitory properties of these compounds on mild steel corrosion in 1 M H_2SO_4. The investigation yielded that the Schiff bases and Pyridinium salts derivatives were successfully synthesized as suggested by the characterization results. Weight loss experiments found that pyridinium salt derivatives exhibited good corrosion efficiency, particularly at 0.01 M. The inhibition efficiencies increased with increasing concentration. Negative values of ΔG° ads imply spontaneous adsorption of organic inhibitors on the surface of steel, as well as indicate adsorption process involving both physisorption and chemisorption. The inhibitors on the metal surface obeyed Langmuir adsorption isotherm. The scanning electron microscope analysis showed the adsorption of inhibitor molecules on the mild steel surfaces and revealed that the mild steel surface was protected in presence of the pyridinium salts derivatives.

References

[1] M. Lagrene, B. Mernari, M. Bouanis, M. Traisnel, F. Bentiss, Corrosion Science/ Study of the mechanism and inhibiting efficiency of 3,5-bis(4-methylthiophenyl)-4H-1,2,4-triazole on mild steel corrosion in acidic media, March 2002, Volume 44/ Issue 3, Pages 573-588. https://doi.org/10.1016/S0010-938X(01)00075-0

[2] J.B. LI, J.E. ZUO, Chinese Journal of Chemistry/ Influences of temperature and pH value on the corrosion behaviors of X80 pipeline steel in carbonate, 26 (2008), Volume26, Issue10 /bicarbonate buffer solution, Pages 1799-1805. https://doi.org/10.1002/cjoc.200890324

[3] R. Samosir, S.L. Simanjuntak, Materials Science and Engineering /The influence of concentration and pH on corrotion rate in stainless steels–316 solution HNO3 medium, 237 (2017) 012047. doi:10.1088/1757-899X/237/1/012047

[4] M.A. Kiani, M.F. Mousavi, S. Ghasemi, M. Shamsipur, S.H. Kazem, Corrosion Science/ Inhibitory effect of some amino acids on corrosion of Pb–Ca–Sn alloy in sulfuric acid solution, , April 2008/ Pages 1035-1045. https://doi.org/10.1016/j.corsci.2007.11.031

[5] Gokhan Gece, Semra Bilgic, Corros. Sci/ Quantum chemical study of some cyclic nitrogen compounds as corrosion inhibitors of steel in NaCl media, 51 (2009), Volume 51, Issue 8/ Pages1876-1878. https://doi.org/10.1016/j.corsci.2009.04.003

[6] Ramazan Solmaz, Ece Altunbas Sahin, Ali Doner, Gulfeza Kardas, Corros. Sci./ The investigation of synergistic inhibition effect of rhodanine and iodide ion on the corrosion of copper in sulphuric acid solution, 53 (2011), Volume 53, Issue 10/ 3231–3240. https://doi.org/10.1016/j.corsci.2011.05.067

[7] Murat Farsak, Hülya Keles, Mustafa Keles, Corros. Sci. / A new corrosion inhibitor for protection of low carbon steel in HCl solution, 98 (2015), Volume 98/ 223–232.

[8] P. Thanapackiam, Subramaniam Rameshkumar, S.S. Subramanian, Kumaravel Mallaiya, Mater. Chem. Phys. / Electrochemical evaluation of inhibition efficiency of ciprofloxacin on the corrosion of copper in acid media, 1 May 2016, Volume 174 / 129–137

[9] K. Ramya, Revathi Mohan, K.K. Anupama, Abraham Joseph, Mater. Chem. Phys. / Electrochemical and theoretical studies on the synergistic interaction and corrosion inhibition of alkyl benzimidazoles and thiosemicarbazide pair on mild steel in hydrochloric acid, (2015), Volumes 149–150 / Pages 632-647

[10] M. Yadav, S. Kumar, R.R. Sinha, I. Bahadur, E.E. Ebenso, J. Mol. Liq./ New pyrimidine derivatives as efficient organic inhibitors on mild

_____

steel corrosion in acidic medium: Electrochemical, SEM, EDX, AFM and DFT studies, (2015) , Volume 211 / 135–145.

[11] F. Touhami, A. Aouniti, Y. Abed, B. Hammouti, S. Kertit, A. Ramdani, K. Elkacemi, Corrosion inhibition of armco iron in 1 M HCl media by new bipyrazolic derivatives, Corros. Sci. 42 (2000) 929–940.

[12] S. Saravanamoorthy, S. Velmathi, Progress in Organic Coatings /Physiochemical interactions of chiral Schiff bases on high carbon steel surface: Corrosion inhibition in acidic media, (2013),76 /1527-1535.

[13] M. Gopiraman, N. Selvakumaran, D. Kesavan, R. Karvembu, Prog. Org. Coat. / Adsorption and corrosion inhibition behaviour of N-(phenylcarbamothioyl) benzamide on mild steel in acidicmedium, (2012), 73 /104–111.

[14] A. Zarrouk, B. Hammouti, H. Zarrok, R. Salghi, A. Dafali, Lh.Bazzi, L. Bammou, S.S. Al-Deyab, Der Pharm. Chem. / Electrochemical impedancespectroscopy and weight loss study for new pyridazine derivativeas inhibitor for copper in nitric acid, (2012), 4 /337–346.

[15] G. K. Sims, L. E. Sommers, Environ. Toxicol. Chem/.Biodegradation of pyridine derivatives in soil suspensions, (1986),5(6) /503-509.

[16] Y. Hamada, in:, P. P. Pandey, (Edt.) /Role of Pyridines in Medicinal Chemistry and Design of BACE1 Inhibitors Possessing a Pyridine Scaffold Pyridine, Pyridine, Chapter 2, BoD- Books on Demand, IntechOpen, London, 2018, pp. 9-26.

[17] R. Hasanov, M. Sadıkoˇglu, S. Bilgic ̧, Appl. Surf. Sci. /Electrochemical andquantum chemical studies of some Schiff bases on the corro-sion of steel in H2SO4solution, (2007), 253/ 3913–3921.

[18] R.A. Prabhu, T.V. Venkatesha, A.V. Shanbhag, G.M. Kulkarni,R.G. Kalkhambkar, Corros.Sci./ Inhibition effects of some Schiff's bases onthe corrosion of mild steel in hydrochloric acid solution, (2008), 50/3356–3362.

[19] ASTM G 31-72, American Society for Testing and Materials,Philadelphia, PA, 1990.

[20] K.S. Jacob, G. Parameswaran, Corrosion Sci./ Corrosion inhibition of mild steel in hydrochloric acid solution by Schiff base furoin thiosemicarbazone, (2010) ,52 /224-228.

[21] Seelam, M., Shaikh, B.V., Tamminana, R., Kammela, P.R., Tetrahedron Letters /An efficient methodology for the synthesis of thioureas from amine mediated by a cobalt source, (2016), Volume 57/ 5297-5300

[22] Abdullah, L. W., Saied, S. M., & Saleh, M. Y. (2021). Deep eutectic solvents (Reline) and Gold Nanoparticles Supported on Titanium Oxide (Au–TiO2) as New Catalysts for synthesis some substituted phenyl (substituted-3-phenyloxiran) methanone Enantioselective Peroxidation. Egyptian Journal of Chemistry, 64(8), 4381-4389.

[23] Govindaraj Saravanan , Veerachamy Alagarsamy, Chinnasamy Rajaram Prakash, Bioorganic & Medicinal Chemistry Letters / Design, synthesis and anticonvulsant activities of novel 1-(substituted/ unsubstituted benzylidene)-4-(4-(6,8-dibromo-2-(methyl/phenyl)- 4-oxoquinazolin-3(4H)-yl)phenyl) semicarbazide derivatives ,(2012), 22 /3072-3078.

[24] Michael B. Smith (Ed.), Organic Synthesis, third ed., Academic Press, 2011.

[25] Ayoob, A., Sadeek, G., Saleh, M. (2022). Synthesis and Biologically Activity of Novel 2-Chloro -3-Formyl -1,5-Naphthyridine Chalcone Derivatives. *Journal of Chemical Health Risks*, 12(1), 73-79. doi: 10.22034/jchr.2022.688560

[26] M.M. Shaban, A.M. Eid, R.K. Farag, et al., Journal of Molecular Liquids/ Novel trimeric cationic pyrdinium surfactants as bi-functional corrosion inhibitors and antiscalants for API 5L X70 carbon steel against oilfield formation water, (2020), Volume 305/ 112817. https://doi.org/10.1016/j.molliq.2020.112817

[27] I.L. Rosenfeld, Corrosion Inhibitors, McGraw-Hill, New York, 1981.

[28] S. Wade, Y. Lizama, Australasian Corrosion Association / Clarke's solution cleaning used for corrosion product removal: efects on carbon steel substrate, in: Corrosion and Prevention, 2015 / Conference Paper - 050, 2015.

[29] ASTM, G1e03: Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, ASTM International, 2004.

[30] A. Kina, J. Ponciano, International Journal of Electrochemical Science/ Inhibition of carbon steel CO2 corrosion in high salinity solutions, (2013), 8 /12600-12612.

[31] M. Fin_sgar, J. Jackson, Corrosion Science/ Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review, (2014), 86/17-41.

_____

[32] ASTM, G4-01, Standard Guide for Conducting Corrosion Tests in Field Applications, ASTM International, 2001.

[33] D.S. Chauhan, K. Ansari, A. Sorour, M. Quraishi, H. Lgaz, R. Salghi, , International Journal of Biological Macromolecules/ Thiosemicarbazide and thiocarbohydrazide functionalized chitosan as ecofriendly corrosion inhibitors for carbon steel in hydrochloric acid solution (2018), 107 / 1747-1757.

[34] J. Haque, V. Srivastava, D.S. Chauhan, H. Lgaz, M.A. Quraishi, ACS Omega 3/ Microwave-induced synthesis of chitosan Schiff bases and their application as novel and green corrosion inhibitors: experimental and theoretical approach, (2018) /5654-5668.

[35] D.K. Yadav, D. Chauhan, I. Ahamad, M. Quraishi, RSC Advances/ Electrochemical behavior of steel/acid interface: adsorption and inhibition effect of oligomeric aniline, (2013), 3 /632-646.

[36] Hassan, Y. I., & Saeed, N. H. (2010). Kinetic study of chlorination of p-methoxyacetanilide by chloramine-T in hydrochloric acid medium. Oriental Journal of Chemistry, 26(2), 415.

[37] V. Srivastava, D.S. Chauhan, P.G. Joshi, V. Maruthapandian, A.A. Sorour, Chemistry Select/ M.A. Quraishi, PEGfunctionalized chitosan: a biological macromolecule as a novel corrosion inhibitor, (2018), 3/ 1990-1998.

[38] Al-Thakafy, N., Al-Enizzi, M., Saleh, M. (2022). Synthesis of new Organic reagent by Vilsmeier − Haack reaction and estimation of pharmaceutical compounds (Mesalazine) containing aromatic amine groups. *Egyptian Journal of Chemistry*, 65(6), 1-2. doi: 10.21608/ejchem.2021.101851.4729

[39] P. Marcus, F.B.Mansfeld, Analytical Methods in Corrosion Science and Engineering, CRC Press, 2005.

[40] sdeek, G., Mauf, R., Saleh, M. (2021). Synthesis and Identification of some new Derivatives Oxazole, Thiazole and Imidazol from Acetyl Cysteine. *Egyptian Journal of Chemistry*, 64(12), 7565-7571. doi: 10.21608/ejchem.2021.88755.4267

[41] N. Baig, D.S. Chauhan, T.A. Saleh, M.A. Quraishi, New Journal of Chemistry / Diethylenetriamine functionalized graphene oxide as a novel corrosion inhibitor for mild steel in hydrochloric acid solutions, (2018), 43/ 2328-2337.

[42] P. Singh, D. Chauhan, S. Chauhan, G. Singh, M. Quraishi, Journal of Molecular Liquids / Chemically modified expired Dapsone drug as environmentally benign corrosion inhibitor for mild steel in sulphuric acid useful for industrial pickling process, (2019), Volume 286 /110903.

[43] Y. Qiang, S. Zhang, S. Yan, X. Zou, S. Chen, Corrosion Science / Three indazole derivatives as corrosion inhibitors of copper in a neutral chloride solution, (2017), 126 /295-304.

[44] Organic Chemistry, Ninth Edition, John McMurry (2015).

[45] C. Kamal, M.G. Sethuraman, Arabian J. Chem. / *Spirulina platensis* − A novel green inhibitor for acid corrosion of mild steel, (2012), 5/155−161.

[46] S. Issaadi, T. Douadi, A. Zouaoui, S. Chafaa, M.A. Khan, G. Bouet, Corros. Sci./ Novel thiophene symmetrical Schiff base compounds as corrosion inhibitor for mild steel in acidic media, (2011) Volume 53/ 1484-1488.

[47] K.R. Ansari, M.A. Quraishi, A. Singh, Corros. Sci. / Schiff's base of pyridyl substituted triazoles as new and effective corrosion inhibitors for mild steel in hydrochloric acid solution, (2014), 79/ 5−15.

[48] I. Jevremović, M. Singer, S. Nešić, V. Miskovic-Stanković, Corros. Sci./ Inhibition properties of self-assembled corrosion inhibitor talloil diethylenetriamine imidazoline for mild steel corrosion in chloride solution saturated with carbon dioxide, (2013), Volume 77/ 265-272. https://doi.org/10.1016/j.corsci.2013.08.012