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Examination the Corrosion Inhibition of Synthesized Azo-Schiff Bases Compounds from (P-Fluorophenyl)-1,3,4-Thiadiazoles for Carbon Steel Alloy in Acidic Medium

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Abstract

New azo-Schiff base compounds were prepared by different processes using (p-fluorophenyl)-1,3,4-thiadiazoles, and their role as corrosion inhibitors for carbon steel alloy in acidic media such as 0.1 M HCl at 298 K was investigated. Spectroscopic methods such as FT-IR and NMR were used to characterise the compounds, and potentiodynamic polarization curves were employed to evaluate their corrosion inhibition. p-Aminoacetophenone was react withed 2-(5-(4-fluorophenyl)-1,3,4-thiadiazol-2-yl) acetohydrazide (A1) to prepare N′ -(1-(4-aminophenyl) ethylidene)-2-(5-(4-fluorophenyl)-1,3,4-thiadiazol-2-yl) acetohydrazide (A2). Azo-Schiff bases (A3-A6) were synthesised by combining the prepared diazonium salts with different phenols. These compounds' structures were changed to improve their ability to prevent corrosion in a range of industrial settings, especially for metals exposed to acidic environments. The inhibitory efficiency percentage was between 76% and 90%. At 90%, the synthetic medication (A6) obtained the highest value. The formed protective adsorption coating on the steel surface was the reason for the improved inhibitor activity. These findings imply that the artificial Azo-Schiff bases show promising application as corrosion inhibitors for carbon steel in acidic settings. Applications in sectors where corrosion resistance is crucial may benefit from this knowledge.

Keywords: *Potentiodynamic; Polarisation; Thiadiazol; Aminoacetophenone; Hydroxy naphthalene; Carbon steel; Fourier Transform Infrared Spectroscopy; Dimethyl sulfoxide.*

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1. Introduction

The chemical, electricity and petroleum industries, frequently use iron and its alloys because of their low cost, strong mechanical properties and simplicity of manufacture [1, 2]. Many industries are affected by the expensive problem of corrosion, especially those that depend on metal parts and buildings that are subjected to severe conditions [3]. Thus, efficient corrosion prevention techniques must be developed. One method is to use anti-corrosion materials. Corrosion inhibitors are classified according to their chemical structure and mechanism, with organic inhibitors being the most common [4-6]. Chemicals known as corrosion inhibitors are used in extreme situations to lessen or prevent metal corrosion. These materials either alter the environment or apply a protective layer to the metal surface to stop corrosion [7]. Their application is essential in industries where metals are regularly subjected to harsh environments, such as those that are acidic, saline or rich in oxygen.

Corrosion inhibitors are essential because they extend the life of metal structures, reduce maintenance and replacement costs and guarantee the safe and dependable operation of industrial systems. They slow down the deterioration of metals and stop the discharge of toxic byproducts into ecosystems, both of which contribute to environmental protection. Hence, they are essential to sectors including construction, chemical processing, water treatment and oil and gas [7-9]. Investigations demonstrated that organic inhibitors comprising heteroatoms such as oxygen, phosphorous, sulphur and nitrogen are exceptionally effective at lowering corrosion in a variety of acidic solutions. Owing to their high polarisability and low electronegativity, these inhibitors function by promoting electron transport to atoms’ vacant orbitals and enabling atoms and functional groups to cover substantial metallic surface regions [10].

Organic compounds, especially derivatives of thiadiazol, have recently attracted attention as possible corrosion inhibitors. Their distinctive molecular structures are characterised by a five-membered heterocyclic ring composed of sulphur and nitrogen atoms [11]. The inclusion of the (p-fluorophenyl) moiety increases the electron density of the thiadiazol ring and may enhance the adsorption characteristics of the resulting Azo-Schiff bases. In acidic media where metal corrosion is most severe, this structural alteration renders these compounds potent corrosion inhibitors [12]. N-heterocyclic compounds can effectively suppress iron or steel corrosion under a wide range of harsh conditions. Many strategies are used to counteract corrosion, each suited to different types of metals and surroundings. Important techniques include passivation, which encourages the production of a persistent oxide layer, mixed inhibition and adsorption inhibition, in which organic inhibitors are adsorbed onto metal surfaces to form protective barriers [13]. One of the best ways to prevent corrosion in metals is to employ inhibitors. Numerous methods have been used to investigate metal corrosion. One of the most practical ways to prevent corrosion in acidic conditions is to utilise chemical inhibitors [14]. The majority of highly effective acid inhibitors are made of organic substances containing sulphur, phosphorus, oxygen and nitrogen. Therefore, research on the connection between adsorption and corrosion inhibition is crucial [15].

The Schiff base, which is the product of the condensation of amines with aldehydes or ketones, has good inhibitive qualities. These ligands are remarkably members of the class in coordination chemistry. Their C=N groups are responsible for this ability. Schiff bases adhere to and shield the metal/solution surface. In this work, azo-Schiff base derivatives were studied to explore their corrosion inhibition of carbon steel in 0.1 M hydrochloric acid solution. Table 2 provides the chemical structures of these derivatives.

The heteroatoms in the heterocyclic structure of N′-(1-(4-((2-amino-4-hydroxyphenyl) diazenyl) phenyl) ethylidene)-2-((5-(4-fluorophenyl)-1,3,4-thiadiazol-2-yl) amino) acetohydrazide (A6) may function as an efficient corrosion inhibitor. Novel azo-Schiff bases were created using p-fluorophenyl-1,3,4-thiadiazoles in order to prevent carbon steel from corroding in acidic settings at room temperature (298 K).

2. Materials and Methods

2.1. Chemicals and Materials

All substances used were supplied by Merck, BDH, Fluka and Sigma–Aldrich Chemicals Companies, Germany. The alloy used in this work was carbon steel (C45) with the following chemical composition:

Table 1,
C45 Carbon steel’s chemical constitution

Metal	C%	Si%	Mn %	S%	P%	Cu%	Ni%	Cr%	Fe%
Carbon Steel 45	0.36-0.42	0.15-0.30	1.00-1.40	0.05	0.05	0.50	0.20	0.20	96.88-97.49

Bruker UltraShield 500 MHz spectrophotometer was used to record NMR (1H-NMR and 13C-NMR) spectral data with DMSO as a solvent at the University of Baghdad’s College of Sciences. A SHIMADZU FT-IR 8300 Fourier transform infrared spectrophotometer was used to calculate infrared spectra for the prepared derivatives as a KBr disc in the wave range of 400–4000 cm^{-1}. A hot stage Gallen Kamp melting point apparatus (m. p.) was used in an open capillary system to determine the melting point. An advanced potentiostat named MLab 200 (2007) bank (Electronic-intelligent controls GmbH) complete with all accessories and three electrode cells was used for polarisation measurements at the

University of Baghdad’s College of Science, Department of Chemistry.

2.2. Measurements and Experimental Setup

2.2.1. Experimental setup

The corrosion inhibition of carbon steel using an organic inhibitor in 0.1 M HCl at 298 K was examined through potentiostat polarisation curves. The experimental setup involved carefully preparing carbon steel specimens by polishing, cleaning and drying to ensure uniformity. The specimens are immersed in an acidic corrosive solution containing the organic inhibitor. A three-electrode electrochemical cell comprising carbon steel as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and platinum as the counter electrode was utilised. Polarisation curves were produced by applying a controlled potential sweep with a potentiostat to investigate anodic and cathodic reactions. The obtained polarisation curves were used to calculate the corrosion rate and effectiveness of the organic inhibitor by determining the corrosion potential (Ecorr), corrosion current density (Icorr) and other electrochemical parameters.

As shown in Figure 1, this configuration offers a thorough assessment of how the organic inhibitor inhibits corrosion in acidic environments by affecting anodic and cathodic corrosion processes.

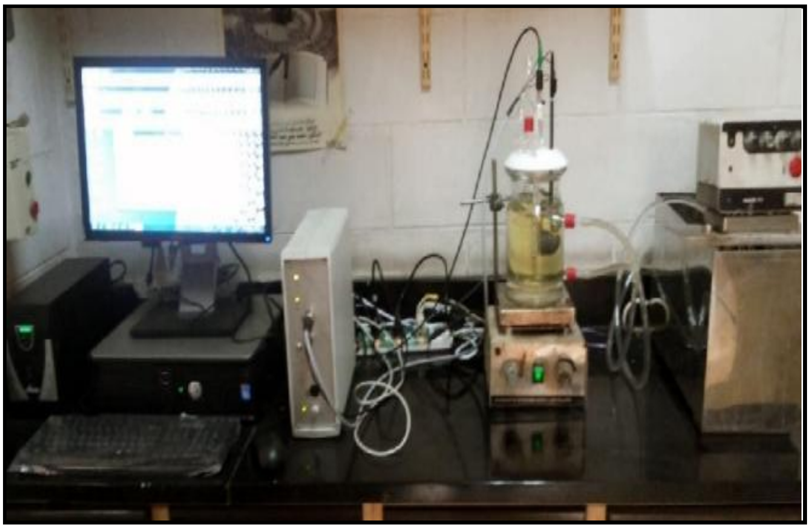


Fig. 1. Complete system set-up for polarisation measurements

An electrochemical cell known as the corrosion cell was used to experimentally evaluate the carbon steel specimens for electrochemical corrosion [16]. The 1 L Pyrex corrosion cell consisted of a three-electrode system whose electrodes (working, axillary and reference) were submerged in an electrolyte solution. (1) Working electrode: The carbon steel specimen served as an electrode during the operation. The metal was reduced or oxidised at the working electrode by an anodic or cathodic process. Studies on corrosion found these reactions to be of interest. (2) Axillary electrode: During the test, the working electrode where the cathodic or anodic reaction occurs was supplied with current by the axillary electrode, which is made of high-purity platinum metal. (3) Reference electrode: A calomel electrode was used to allow the potentiostat to regulate the voltage between the working and reference electrodes. The login tube serves as a salt bridge, minimises the potential drop caused by resistance at the interface between the working electrode and the electrolyte and controls the reference electrode’s ideal location.

2.2.2. Synthesis of inhibitors

a) Synthesis of N′-(1-(4-aminophenyl) ethylidene)-2-((5-(4-fluorophenyl)-1,3,4-thiadiazol-2-yl) amino) acetohydrazide (A2) [17, 18]: 20 mL of 100% ethanol was used to dissolve compound (A1) (0.5 g, 0.001 mol). Glycolate acetic acid and p-aminoacetophenone were added in small amounts to this solution (0.03). For 10 hours, this combination underwent reflux. The precipitate was removed from the ethanol by filtering, drying and recrystallisation after cooling (A2) (85% yield, mature point (m. p.) ٤٧١.15 k–473.15 k, yellow precipitation; m. p. 478.15 k–480 k, yield 96%, yellow precipitate).

b) General synthesis method for azo-Schiff bases (A3–A6) [19, 20]: After dissolving compound A2 (0.007 mol) in 15 mL of concentrated HCl and 15 mL of distilled water, the mixture was cooled in an ice bath until it reached a temperature between 0 and 278.15 k. The $NaNO_2$ solution, which was prepared by dissolving 0.47 g or 0.007 mol into 5 mL of distilled water, was dropwise added to the reaction mixture, which was then agitated for 10 minutes. The mixture was slowly and carefully added to a solution containing various phenols (0.007 mol) such as phenol, β-naphthol, p-nitrophenol, salcildehyde and 3-aminophenol in 60 mL of 10% NaOH at 0–278.15 k. The mixture was then agitated for 30 minutes. Hot steam was used to dry the coloured product after it was filtered and cleaned with cooled distilled water.

N′-(1-(4-((2-hydroxynaphthalen-1-yl) diazenyl) phenyl) ethylidene)-2-((5-(4-flourophenyl)-1,3,4-thiadiazol-2-yl) amino) acetohydrazide (A3):
yield 70%, m. p. 363.15 k–365.15 k, burgundy precipitate

N′-(1-(4-((2-hydroxy-5-nitrophenyl) diazenyl) phenyl) ethylidene)-2-((5-(4-flourophenyl)-1, 3, 4-thiadiazol-2-yl) amino) acetohydrazide (A4): yield 80 %, m. p. 506.15 k–508.15 k, pale orange precipitate

N′-(1-(4-((3-formyl-4-hydroxyphenyl) diazenyl) phenyl) ethylidene)-2-((5-(4-flourophenyl)-1, 3, 4-thiadiazol-2-yl) amino) acetohydrazide (A5): yield 83%, gummy, greenish brown precipitate

N′-(1-(4-((2-amino-4-hydroxyphenyl) diazenyl) phenyl) ethylidene)-2-((5-(4-flouro phenyl)-1, 3, 4-thiadiazol-2-yl) amino) acetohydrazide (A6): yield 82%, m. p. 430.15 k–432.15 k, orange precipitate

2.3. Corrosion Measurement

Carbon steel alloy was utilised, and its chemical composition is detailed in Table 1. Before the corrosion test, the carbon steel electrode underwent polishing with emery papers grade 800–1200. Distilled water, acetone and alcohol were used for ultrasonic cleaning, followed by drying in dry air. A 0.1 M HCl aqueous solution, the testing electrolyte, was prepared by diluting AnalaR grade 37% HCl with ultrapure water.

Polarisation measurements were conducted using a standard corrosion cell. The setup included a corrosion cell with three electrodes: a working electrode made of carbon steel alloy, a counter electrode and a reference electrode SCE. All potential values were referenced to the SCE. Electrochemical experiments were performed over a potential range of 200 mV. Before measurements, the working electrode was immersed in the test solution for 900 seconds to achieve a steady-state open circuit potential (Eocp). All tests were carried out at 298 K using a cooling or heating circulating water bath [21].

3. Results and Discussion

3.1. Synthesis and Analysis

The Azo-Schiff base compounds produced from (p-fluorophenyl)-1,3,4-thiadiazoles were studied using analytical techniques, FT-IR and NMR. The FT-IR spectra of the compounds (A3–A6) in Figures 4–10 confirmed the formation of azo dyes via the appearance of a stretching band of OH at 3200–3433 cm^{-1} [3]. FT-IR spectral data also showed the appearance of a stretching band of N=N at 1425 cm^{-1}. All details of the FTIR spectral data of compounds A3–A6 are listed in Table 2. The presence of distinctive C=N stretching vibrations in the FT-IR spectra verified the synthesis of Schiff bases. The molecular structure was revealed by NMR spectroscopy, which also verified that the p-fluorophenyl group was successfully incorporated into the 1,3,4-thiadiazole ring. Compounds A3 and A5) were identified by 1HNMR and 13CNMR: new values appeared at δ = 13.03–13.13 ppm attributed to the OH proton, and a new signal at δ = 1.13, 1.17 ppm indicated binding the (CH3) group of compounds (A3, A5). In contrast, the 13CNMR spectrum of compound A3 displayed characteristic signals δ (ppm) at 39.7, 154.38 and 170.34 attributed to CH3, (C-OH) and (C=N), receptively. The 1HNMR and 13CNMR spectra of compounds A3 and A5 are listed in Tables 3 and 4 and displayed in Figures 8–10.

Table 2,
FTIR spectral data of compounds A3–A6

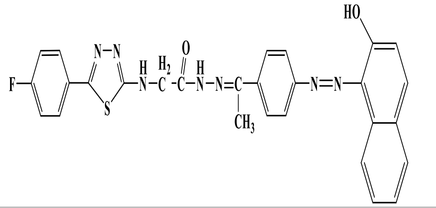
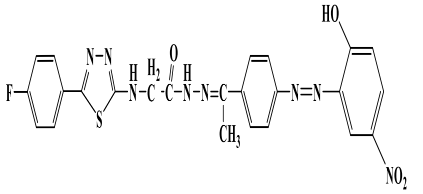
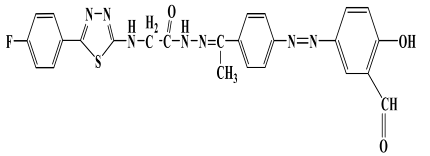
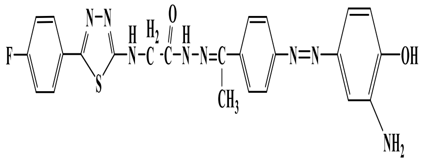
Com. NO.	Str.	**FTIR spectral data cm^{-1}**						
		N (N-H)	**ν(C-H) aroma.**	**N (C-H) alipha.**	**ν(C=N)**	**ν(C=O)**	**ν(N=N)**	**Others**
A3		3180	3064	2887	1623	1689	1425	(C-F) 1296 (OH) 3200
A4		3269	3064	2920 2854	1602	1687	1425	(C-F) 1292 (OH) 3433
A5		3101	3064	2960, 2827	1687	1604	1425	(C-F) 1286
A6		3200	3064	2960 2885	1687	1602	1425	(C-F) 1288

Table 3,
^{1}HNMR spectral data (δ ppm) of compounds A3 and A5

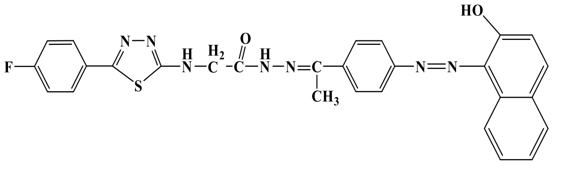
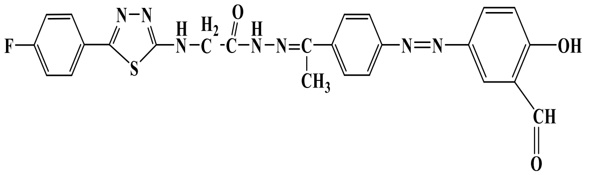
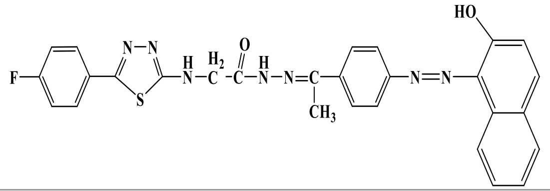
Com. No.	**Structure**	**1HNMR spectral data (δ ppm)**
A3		1.13 (s, 3H, -CH3); 2.53 (d, 2H, -CH2); 7.80 (s, H, NH); 6.36-8.89 (m, 14H, CH-Ar); 13.13 (s, H, OH)
A5		1.13 (s, 3H, -CH3); 2.8 (d, 2H, -CH2); 7.41 (s, H, NH); 6.36-8.58 (m, 14H, CH-Ar); 10.12 (s, H-C=O); 13.03 (s, H, OH)

Table 4,
^{13}CNMR spectral data (δ ppm) of compound A3

Com.	**Structure**	**13CNMR spectral data (δ ppm)**
A3		39.7 (CH3); 124.90-129.37 (C-Ar); 136.47 (C-CH3); 148.16 (C-F); 154.38 (C-OH); 170.34 (C=N)

3.2. Potentiodynamic Polarisation Measurements

The corrosion inhibition performance of the synthesised compounds was evaluated by conducting potentiodynamic polarisation in acidic media. Table 2 shows that compared with that in the blank solution, the corrosion current density (Icorr) in the presence of the azo-Schiff base inhibitors significantly decrease from 563.2 µA/cm2 to 137.3, 102.0, 74.28 and 56.26 µA/cm2 for A4, A3, A6 and A5, respectively. The decrease in corrosion rate corresponded to an inhibitory efficiency percentage (IE%) of 90% for compound A5 as shown in Figure 2 and Table 5.

$$\%\mathrm{IE} = \frac{(\mathrm{icorr})\mathrm{o} - (\mathrm{icorr})}{(\mathrm{icorr})\mathrm{o}} * 100, \qquad (1)$$

where (i corr) is the corrosion current density in the absence of inhibitors, (icorr) is the corrosion current density in the presence of inhibitors [22, 23].

Figure 1 shows the polarisation curves of the blank and inhibited solutions with different synthesised compounds. The extent of rusting in 0.1 M HCl solution and the cathodic and anodic Tafel slopes in the presence and absence of the inhibitor molecules were extrapolated. The current corrosion density (Icorr) and corrosion potential (Ecorr) were calculated. Table 5 displays the calculated corrosion potential (Ecorr, mV), corrosion current density score (A/cm2), cathodic and anodic Tafel slopes (mV/Dec) and protection effectiveness PE% [24]. The corrosion potential (Ecorr) shifted to a more active potential for all the compounds, indicating a change in the natural surface. As a result, the inhibitors were adsorbed on the carbon steel surface. The anodic (βa) and cathodic (βc) slopes were changed significantly (Table 5 and Figure 2, indicating that the compounds act as a mixed-type inhibitor affecting anodic and cathodic reactions.

Table 5,
Corrosion parameters for blank and compound in HCl solutions and different compounds.

Comp.	Blank	A3	A4	A5	A6
-Ecorr (V)	-0.385	-0.717	-0.743	-0.862	-0.812
Icorr (µA/cm^2)	563.2	102.0	137.3	56.26	74.28
I corr./ r (A/cm^2)	0.001	2.040E-4	2.747E-4	1.125E-4	1.486E-4
Resis. (Ω)	28.96	1209	955.8	1836	1842
-Bc (mV/Dec)	0.055	0.502	0.561	0.577	0.722
Ba (mV/Dec)	0.120	0.655	0.656	0.405	0.559
Corr. rate, (mm/y)	5.529	1.001	1.348	0.552	0.729
IE%	-	82	76	90	87

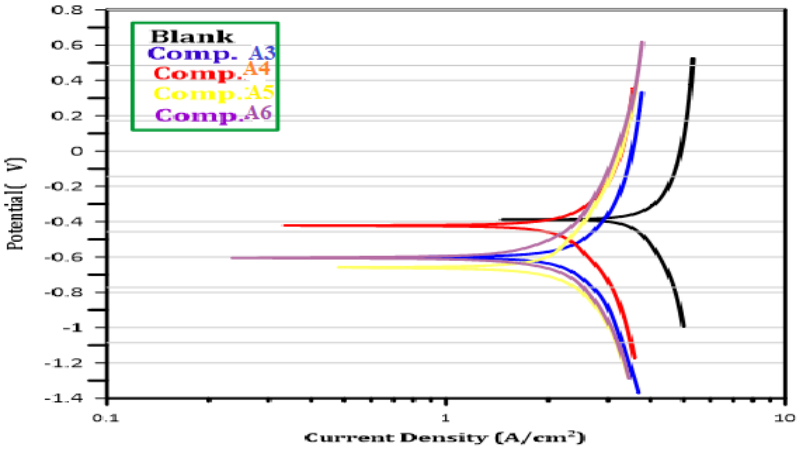
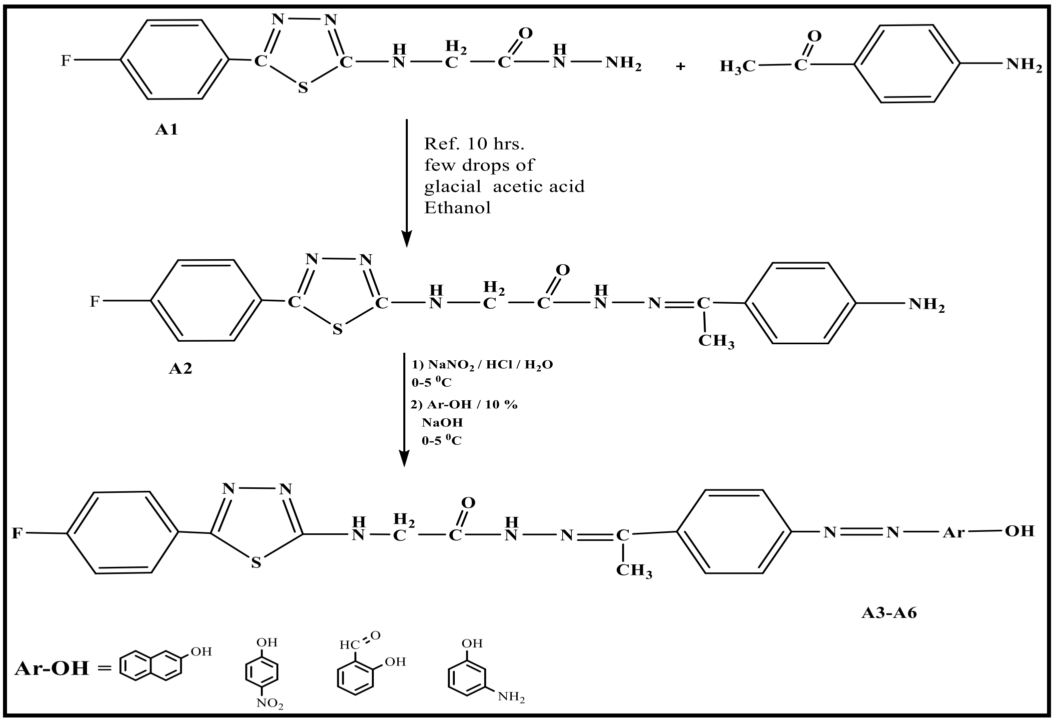


Fig. 2. Polarisation curve of carbon steel in 0.1 M HCl and inhibited solutions with four synthesised compounds (A3, A4, A5 and A6) at 298 K

3.3. Mechanism of Inhibition

The inhibitory effectiveness of the heteroatoms followed the sequence O < N < S, which is attributed to the presence of C=N groupings. Azo-Schiff bases demonstrate their inhibitory effectiveness mainly through their adsorption on the metal/solution interface [3, 25], creating a barrier that keeps corrosive substances from getting to the metal. The lone pair electrons on the Schiff base's nitrogen atoms and the π-electrons of the aromatic rings, which interact with the metal surface, are probably involved in the adsorption process. By increasing the electron density surrounding the Schiff base, the use of a p-fluorophenyl group leads to good adsorption and high inhibitory efficiency. Additionally, the p-fluorophenyl group's electron-donating action is probably responsible for the observed rise and fall in Icorr values [26].



Scheme 1. Synthesis route of compounds A3–A6

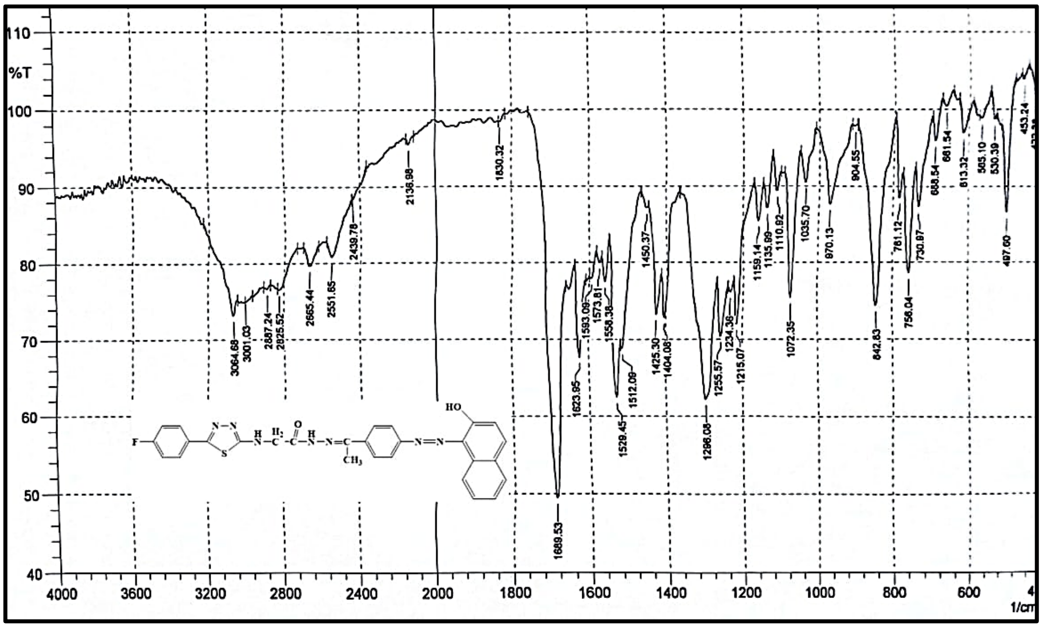


Fig. 3. FTIR spectrum of compound A3

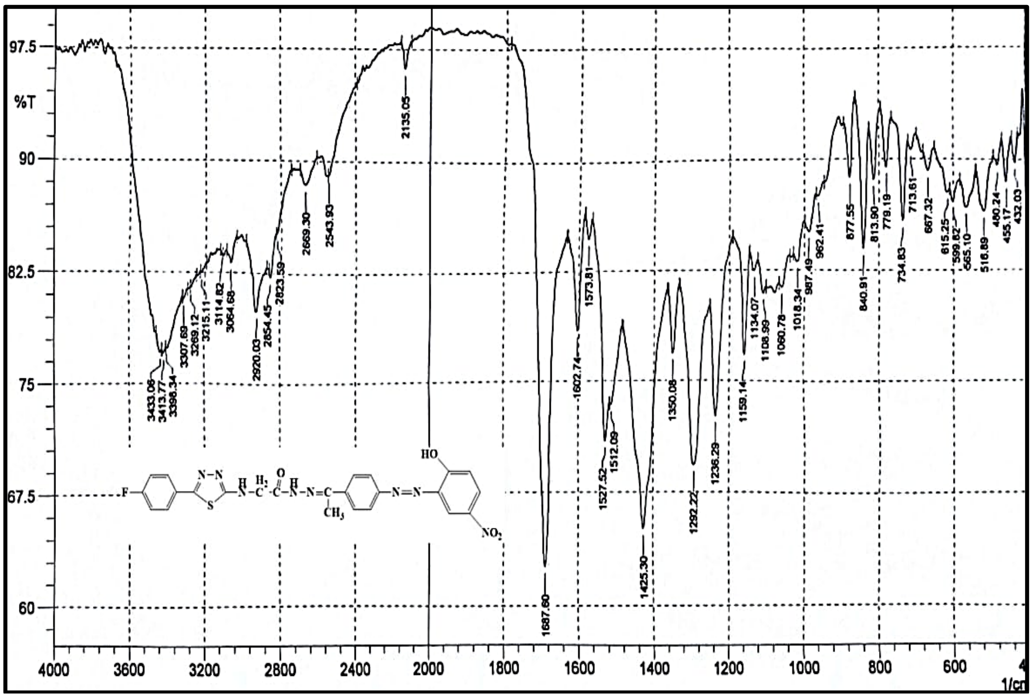


Fig. 4. FTIR spectrum of compound A4

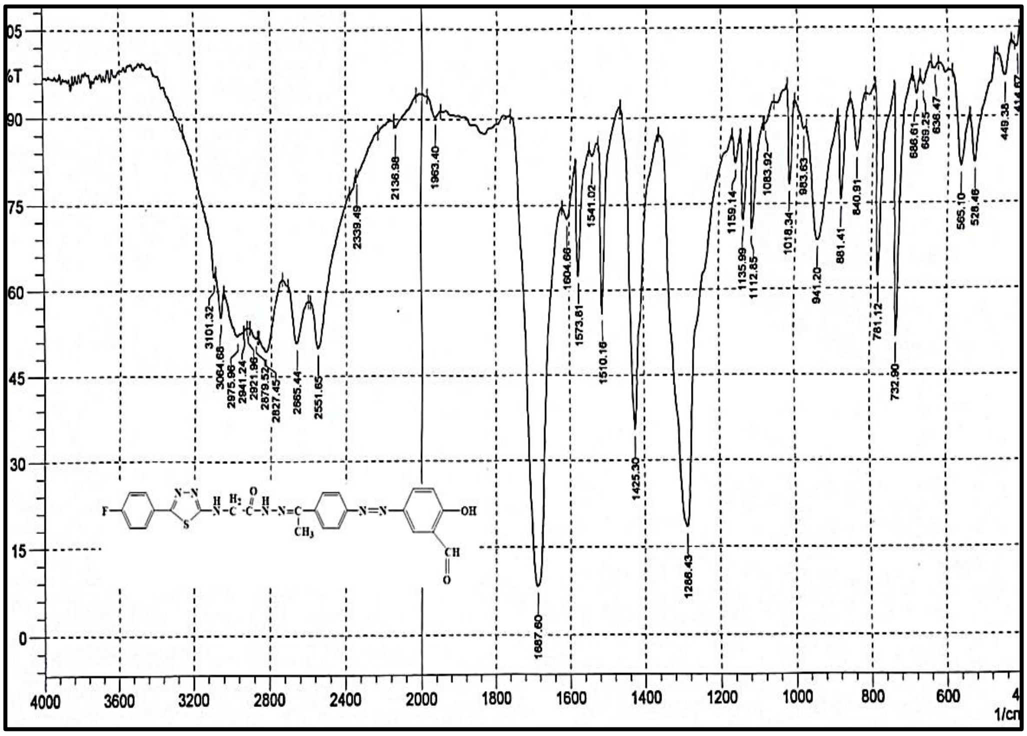


Fig. 5. FT-IR spectrum of compound A5

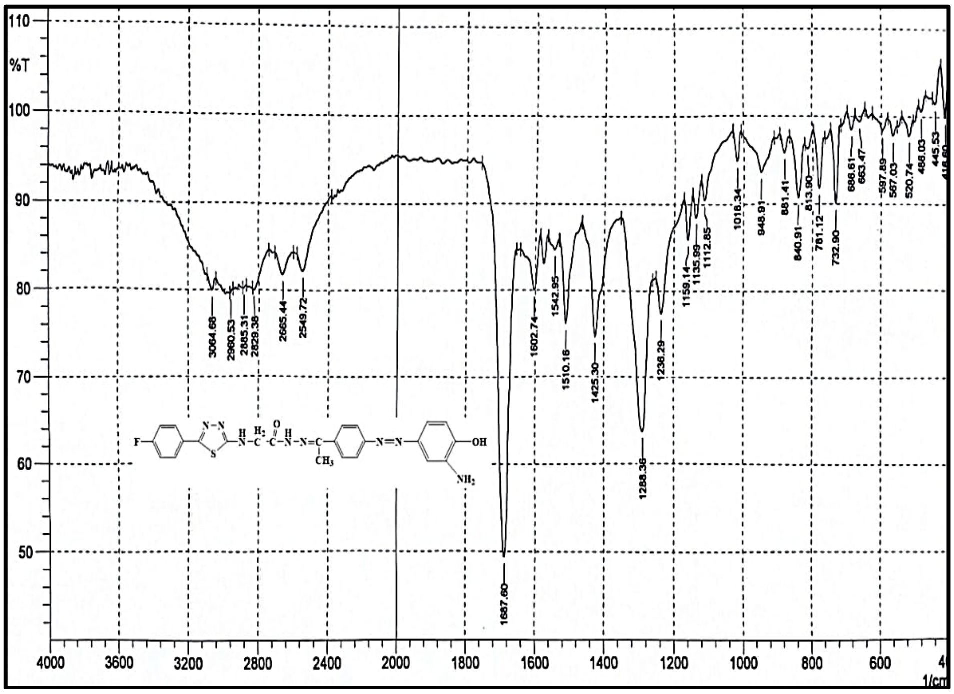


Fig. 6. FT-IR spectrum of compound A6

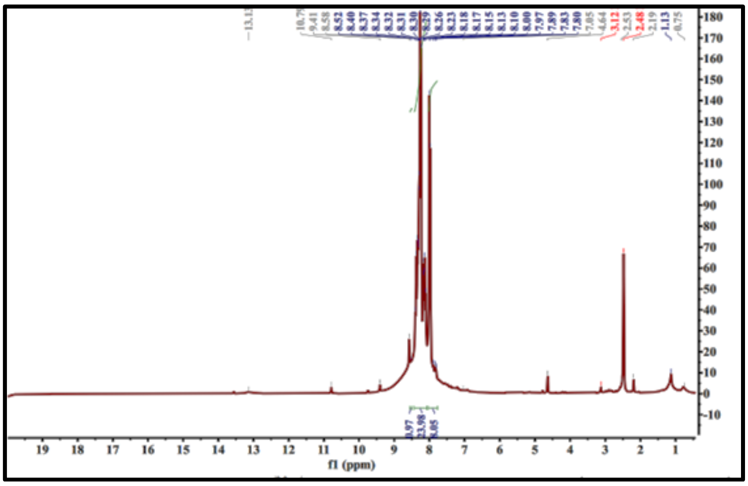


Fig. 7. 1HNMR spectral data of compound A3

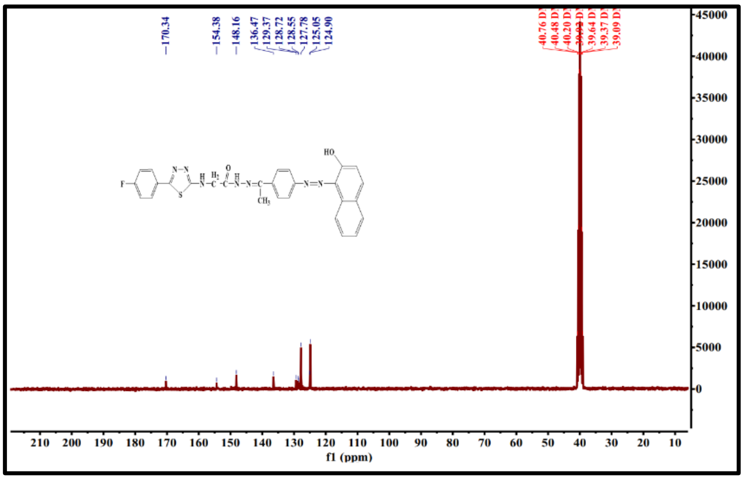


Fig. 8. 13CNMR spectrum of compound A3

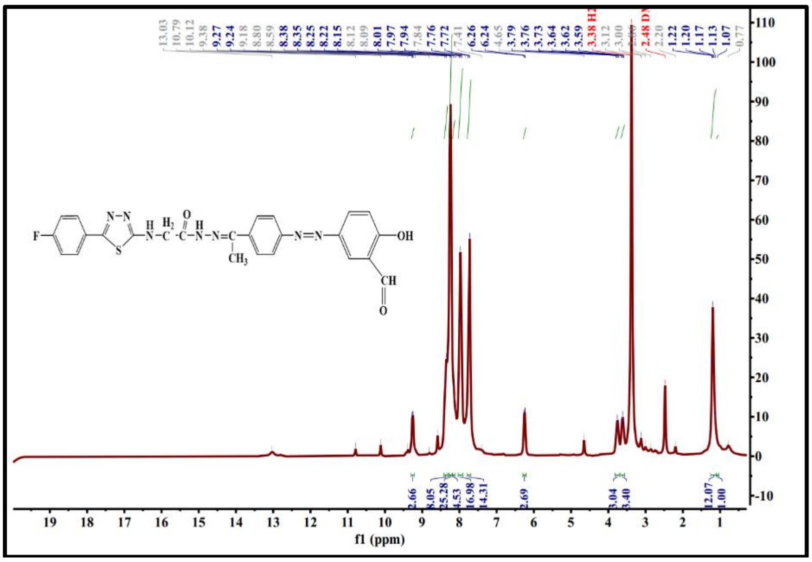


Fig. 9. 1HNMR spectrum of compound A5

4. Conclusions

Azo-Schiff base compounds were synthesised from (p-fluorophenyl)-1,3,4-thiadiazoles, and their potential as potent corrosion inhibitors for metallic materials in acidic environments was assessed. Their structures were confirmed using FT-IR, ^{1}H NMR and ^{13}C NMR. Compounds A3–A6 were evaluated for their capacity to prevent the surface corrosion of carbon steel in an acidic environment. These substances showed potent anticorrosive properties by forming an adsorbed layer on the carbon steel's surface. The synthetic Azo-Schiff bases exhibited improved structural properties, particularly stability and adsorption capacity for the p-fluorophenyl moiety on the metal substrate. These improvements led to a high inhibition efficiency, demonstrating the ability of these compounds to stop metal corrosion.

The findings highlight the importance of molecular design in creating potent corrosion inhibitors. The Azo-Schiff base compounds derived from (p-fluorophenyl)-1,3,4-thiadiazoles provide good corrosion protection and are an eco-friendly substitute for traditional inhibitors. This research advances our knowledge of the mechanisms underlying corrosion inhibition and encourages the development of creative, long-lasting corrosion prevention techniques. Future studies should concentrate on enhancing the structural properties of these materials and analysing their performance in various industrial environments. Comprehensive investigations on the stability and environmental impact of these inhibitors would be beneficial to guarantee legal compliance and real-world use.

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دراسة تثبيط التآكل لمركبات قواعد الآزو شيف المحضرة من (ب-فلوروفينيل) -١,٣,٤- ثياديازول لسبيكة الفولاذ الكربوني في الوسط الحمضي

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المستخلص

تم التحضير لمركبات قواعد آزو-شيف بطرق مختلفة، وثمت دراسة قواعدها كمثبطات التآكل لسبائك الفولاذ الكربوني في حامض الهيدروكلوريك بتركيز ٠,١ مولاري عند درجة حرارة ٢٩٨ كلفن في الوسط الحامضي. حُضِّرت المركبات الجديدة باستخدام (بارا-فلوروفينيل)-١،٣،٤-ثياديازول، وطرق طيفية مثل تحويل فورييه للأشعة تحت الحمراء والرنين المغناطيسي النووي لتحديد هوية المركبات، ومنحنيات الاستقطاب الجهدي الديناميكي لمعرفة مدى فعالية تثبيط التآكل. يتفاعل بارا-أمينوأسيتوفينون مع ٢-(٥-(٤-فلوروفينيل)-١،٣،٤-ثياديازول-٢-يل) أسيتوهيدرازيد (A1) لتحضير N'-(١-(٤-أمينوفينيل) إيثيليدين)-٢-(٥-(٤-فلوروفينيل)-١،٣،٤-ثياديازول-٢-يل) أسيتوهيدرازيد (A2). صُنعت قواعد آزو-شيف (A3-A6) من أملاح الديازونيوم المُحضرة مع فينولات مختلفة. حُوِّلت تركيبات هذه المركبات لتحسين قدرتها على منع التآكل في مجموعة من البيئات الصناعية، وخاصةً للمعادن المعرضة للبيئات الحمضية. تراوح نطاق نسبة الكفاءة المثبطة (IE%) بين ٧٦٪ و٩٠٪. عند ٩٠٪، حقق الدواء الاصطناعي (A6) أعلى قيمة. ويُعزى تحسن نشاط المثبط إلى تكوين طبقات امتزاز واقية على سطح الفولاذ. تشير هذه النتائج إلى أن قواعد آزو-شيف الاصطناعية واعدة جدًا للاستخدام كمثبطات تآكل الفولاذ الكربوني في البيئات الحمضية. وقد تستفيد التطبيقات في القطاعات التي تُعد فيها مقاومة التآكل أمرًا بالغ الأهمية من هذه المعرفة.

في هذا البحث تم تصنيع مركبات قاعدة الآزو-شيف من (p-fluorophenyl) -1,3,4-thiadiasols واستخدمت عند درجة حرارة ٢٩٨ كلفن في الهايدروكلوريك ٠,١ مولاري كمثبطات تآكل لسبيكة الفولاذ الكربوني. تمت دراسة تآكل الفولاذ الكربوني في الظروف الحامضية باستخدام منحنى الاستقطاب الديناميكي. يتكثف بارا-أمينو أسيتوفينون والمركب (A1) ليشكل-N' (١-(٤-أمينو فينيل) إيثيليدين)-٢-(٥-(٤-فلوروفينيل) أسيتوهيدرازيد (١,٣,٤-ثياديازول-٢-بيل (A2) (خضعت أملاح الديازونيوم المحضرة والفينولات المختلفة لعملية اقتران لتكوين قواعد آزو شيف (A3-A6) وخضعت هذه المواد لتعديلات هيكلية لتحسين كفاءتها كمثبطات للتآكل في مجموعة من البيئات الصناعية، خاصة بالنسبة للمعادن المعرضة للتآكل. أشارت النتائج إلى أن نسبة كفاءة التثبيط (IE%) تراوحت بين ٧٦٪ إلى ٩٠٪، وكانت المادة الكيميائية (A6) هي الأعلى قيمة وهي ٩٠٪ على السطح الفولاذي، وتكونت طبقات امتصاص وقائية وهي المسؤولة لأداء المانع الجيد.