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Synthesis, Characterization and Corrosion Inhibition of Novel Pyridine on Mild Steel in Hydrochloric Acid Environment

Basma A. Hadi*, Hiba H. Ibraheem*

Department of Applied Sciences, University of Technology – Iraq

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Corresponding Author:
Hiba H. Ibraheem
as.19.07@grad.uotechnology.edu.iq

Abstract

Corrosion inhibitions in corrosive solutions of hydrochloric acid for mild steel by chemical compound 3-acetyl-4-(4-bromophenyl)-6-2-oxo-2H-chromen-3-yl pyridine-2(1H)-one (ABCP), was conducted and the chemical structure was elucidated The Nuclear Magnetic Resonance (H-NMR) and Fourier Transform Infrared (FT-IR) spectroscopic techniques. The compound ABCP had been investigated at 25 ˚C via weight loss technique. The outcomes show that the ABCP displays great performances as an inhibitor for mild steel in 0.5 M hydrochloric acid. Inhibition efficiency increments with expanding of concentration and become 98.4% at the highest studied concentration. The studies have demonstrated a reverse association between corrosion rate (CR) and inhibition efficiency (IE percent), as IE increases while CR decreases with an increased concentration. In the presence of ABCP, inhibitory efficiency was up to 98.4% at 25°C in presence of ABCP (0.5 mM). IE drops notably at 65°C with an increased temperature. By means of FT -IR and NMR spectroscopy approaches and physical properties through melting point and Thin Layer Chromatography (TLC), the chemical structure of the tested inhibitor has been clarified.

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1. Introduction

The impairment of a metal surface by corrosion is an inevitable consequence of the slow continuous oxidation and reduction reactions in many circumstances [1]. Corrosion of metals is a constant and continuous problem, often difficult to eliminate [2]. An organic inhibitor acts as a good inhibitor among other corrosion inhibitors because it contains heteroatoms such as sulphur, nitrogen, and oxygen in addition to the presence of aromatic rings. The organic inhibitor acts through adsorption on metal surfaces by forming a layer which that prevent the attack of acid media to metal surfaces [3]. Block active areas and so reduce the process of corrosion. Organic inhibitors have their efficiency attributable to their molecular structures, functional groups, chain bonding capabilities, aromaticity and strength of binding between inhibitors and metals. The organic inhibitor's molecular structure and electronic features make it possible to adsorb the metal surfaces highly important. Based on their chemical structure, functional groups, connection capacity, the aromaticity, and inhibitor-metal interaction strength, the efficacy of organic inhibitors was determined. Organic inhibitors have a major role in aiding their adsorption on metal surfaces because of their molecular structure and electrical properties [4]. Researchers in corrosion and industry often find organic compounds with possible inhibitory properties, inexpensive, non-toxic, and dissolving into water-based Metals used for industrial processes are regulated or decreased by corrosion solutions [5].

Furthermore, in the corrosion studies, the selection of a suitable corrosion inhibitor manages its cost-effectiveness, its material efficiency and its environmental side-effects. The majority of synthetic composites are very harmful to individuals and the environment, though [6]. In addition, excellent anti-corrosion compounds for metals in hydrochloric acid are nitrogen-containing organic inhibitors. In acidic mediums, steel alloys react easily and become a substantial economic loss from metallic to ionic state, Corrosion inhibitors may be classed by chemical structure, action mode, etc. Organic corrosion inhibitors are one of the prevalent groups, and they have gained the greatest significance thanks to their easily synthesized and affordable costs. The performance of inhibitors with various heteroatoms frequently follows the reverse sequence of electronegativity so that o<N<S<P in S, N, O and P are achieved [7][8].

The objective of the present research is to assess, using gravimetric techniques (weight loss) under varied temperatures and inhibitor concentrations, the corrosion inhibitory effectiveness of pyridine derivative for mild steels in a corrosive solvent. Surround evaluate the protective inhibitor plot of mild steel coupons in presence of a pyridine derivative.

2. Method and Experimental Procedure

2.1. Synthesis and Characterization of ABCP

The mixture of (3-acetylcoumarin) (0,01 mol) [9], aldehyde (4-bromo benzaldehyde) (0.01 mol), ethyl acetoacetate (0.01 mol), and ammonium acetate (0.08 mol) in (10 ml) ethanol was refluxed for 24 hrs. [10][11][12]. The progress of the reaction was monitored by TLC (hexane: ethyl acetate, 7:3, Retention Factor (RF) = 0.51 [13]. The resulting mixture was then filtered and recrystallized from the ethanol. The yield was 68% and the melting point (288 to 286)°C. Analysis of Fourier Transform Infrared Spectroscopy (FT-IR) showed: peak of 1720,56 cm^{-1} (ketone-carbonyl), 1674,27 cm^{-1} (coumarin-carbonyl), 1627,97 cm^{-1} (amide-carbonyl), 3269,45 cm^{-1} (amino-group) and 3176 cm^{-1} (C-H aromatic) as shown in figure 1. The Nuclear Magnetic Resonance (NMR) in DMSO-d6: δ = 2.53 ppm (s , 3H, CH3), 7.41-8.99 ppm (m,10H, Ar-H, c-H aryl of lactone ring and C-H aryl of pyridine ring), 11,19 (s,1H, N-H) as shown in fig. 2.

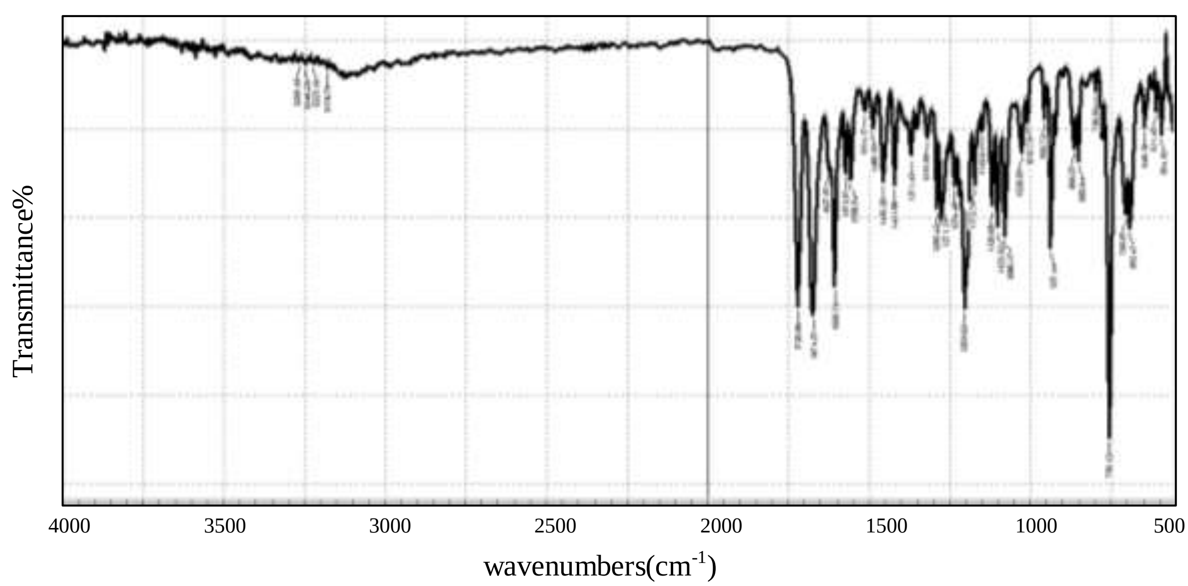

Figure 1: Fourier Transform Infrared Spectroscopy (FT-IR) of ABCP.

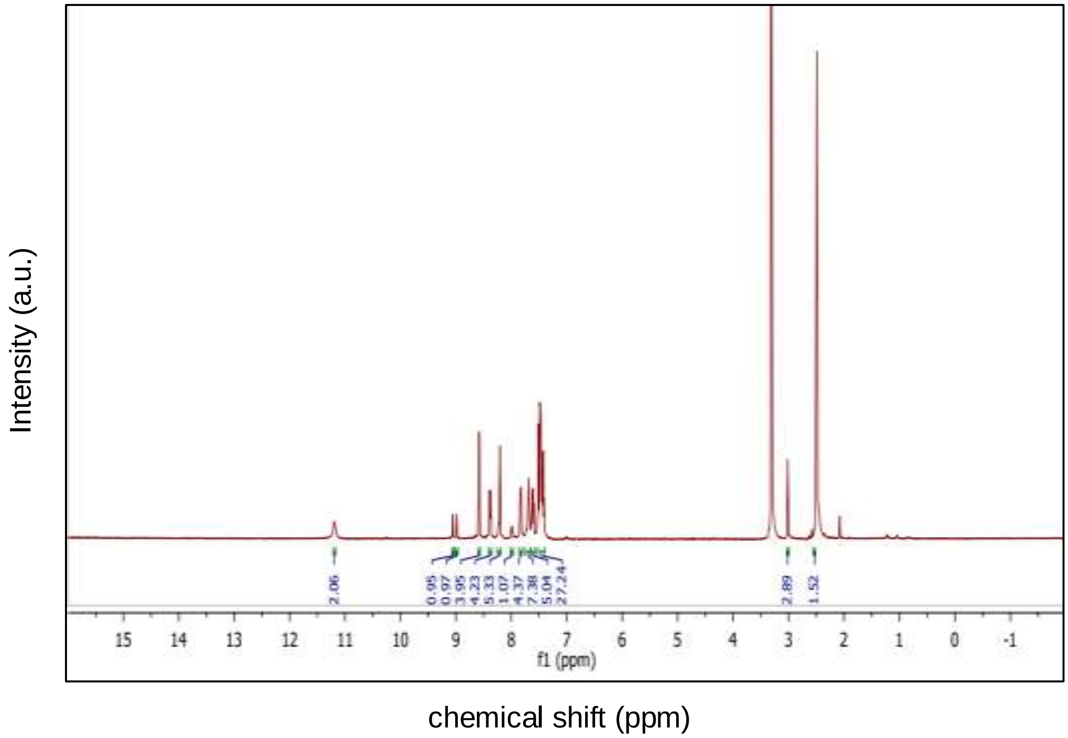

Figure 2: The [1]H-NMR spectrum of ABCP.

2.2. Solutions

The 0.5 M hydrochloric acid corrosive environment required for the corrosion inhibition tests was generated by the addition of hydrochloric acid (HCl) 37 per cent analytical grade to the deionized water. Corrosion inhibitor dissolving in 0.001,0.002,0.003,0.004,0.005 M was employed for the production of quantities of inhibiter-soluble solutions [13][14].

2.3. Weight Loss Measurements

Coupons of mild steel with dimensions 1.7x 1.7 x 0.1 cm^3 were utilized for gravimetrical techniques.. The tested coupon was previously abraded with varied degree silicon carbide sheets rinsed water with double distillation and then acetone dried. For each test coupon, The weight has been calculated. Due to the use of fishing lines and varied APCB concentrations, mild steel vouchers had been immersed into a corrosive environment at different temperatures (25,35.45,55,65 °C). After 3, 6, 12, 24, 48 and 72 h. the weight loss for mild steel cuts was measured [15]. Application Equations were calculated for the (CR) [2], inhibitory efficiency (IE) [16] and Surface coverage degree (θ) [17] was measured by the application of equations:

$$CR = \Delta W / S.t \qquad (1)$$

If − ΔW is the loss of weight (mg), S is the mild steel area (cm^{-2}) and t is the immersion period (h^{-1})

$$IE\,(\%) = (CR - CRi / CR) * 100 \qquad (2)$$

In the absence of the inhibitor tested, where the CR shall be the CR, CR(i) shall be the CR in the presence of the inhibitor tested.

MS surface coverage (θ) was calculated using Eq. 3.

$$\theta = CR - CRi / CR \qquad (3)$$

3. Results and Discussion

3.1. Chemistry

ABCP synthesis was performed through refluxation of 3-acetyl coumarin in ethanol with enough aldehyde (4-bromon benzaldehyde), ethyl acetoacetate. The process is ended by removing the water molecule and producing ABCP at a rate of 68%. (Figure 1)

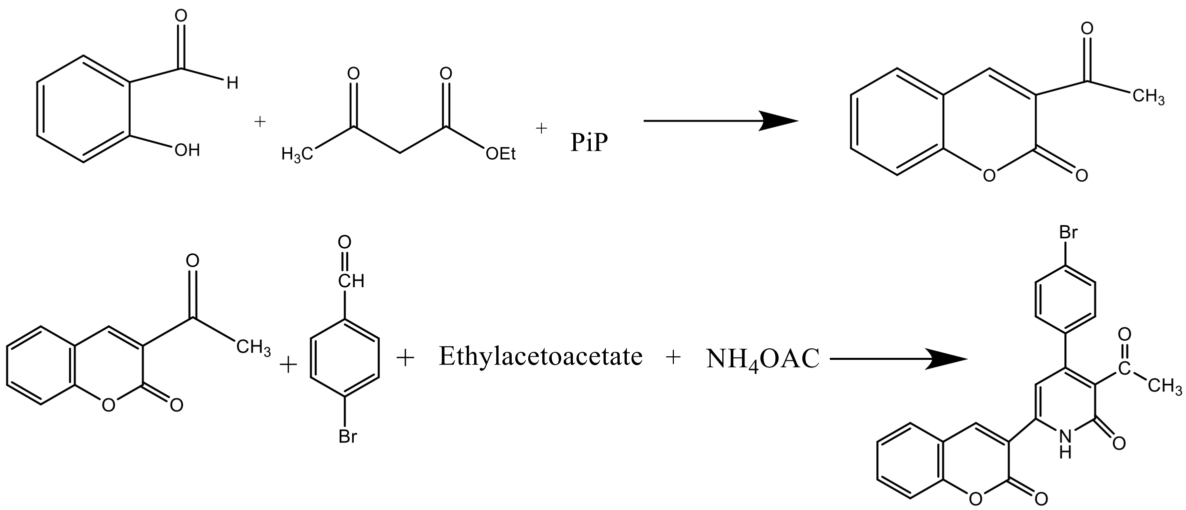

Figure 3. The reaction synthesis of ABCP.

3.2. Weight Loss Tests

Weight loss of mild steel coupons was tested at different temperatures (25, 35, 45, 55, and 65 OC). after exposures at different durations (3, 6, 12, 24 and 72 hours).

3.3. Weight Loss-Concentration Effect

The ABCP study reduces the low and high concentration of mild steel corrosion at 25 ^{o}C in corrosive environments. The corrosion rate vs the concentration of the inhibitor is shown to gradually Reduce the rate of corrosion (mg.cm^{-2}.h^{-1}), as shown in figure 2. With the increased inhibitor concentration, the inhibitory performance was increased. At the ABCP concentration of 0.005 M, shown in figure 4, At the ABCP concentration of 0.005 M as shown in figure 5, the maximum inhibitory efficiency was 98.37 %. It is shown that ABCP reduces and controls the corrosion of mild steel at all the concentrations in the study. The surface of mild steel is responsible for the adsorption of the ABCP molecules. This adsorption decreases a mild steel dissolving and increases its inhibitory effectiveness by blocking the sites.

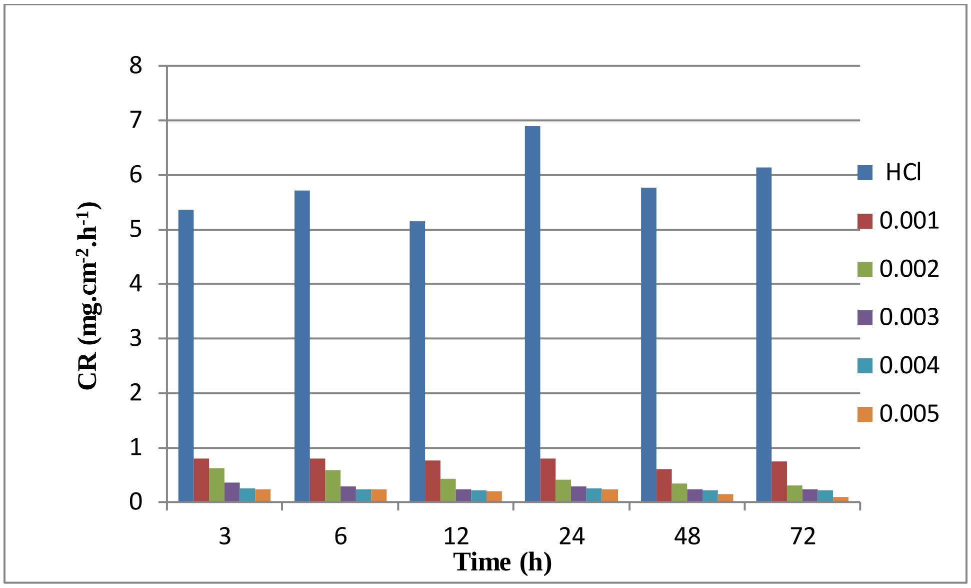

Figure 4: Corrosion rate for diverse immersion time at different concentrations of ABCP.

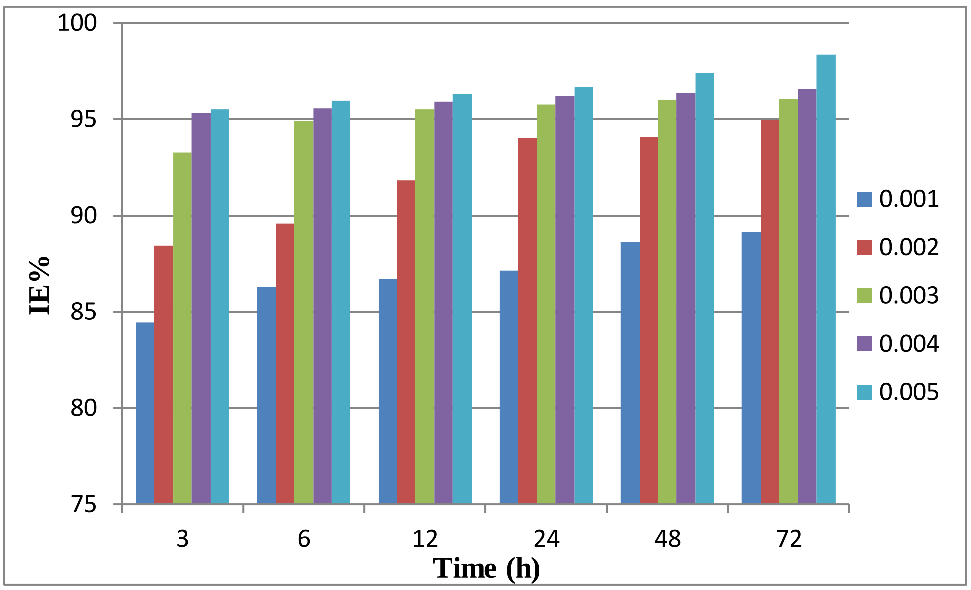

Figure 5: Inhibition Efficiency of different ABCP concentrations at different times of immersion.

3.4. Weight Loss-Temperature Effect

Figure 6. illustrates the inhibitory efficiency at various temperatures (25,35,45,55,65 ° C). Results indicate a reduction in the corrosion of mild steel coupons due to the presence of ABCP molecules. The inhibitory efficiency has increased as demonstrated when the ABCP concentration is raised. Increased temperature, it was noticed that the inhibitions the effectiveness of the inhibitors decreased even with the growing ABCP concentration when temperatures increased. The ABCP molecules on the mild steel surface can be owing to the desorption.

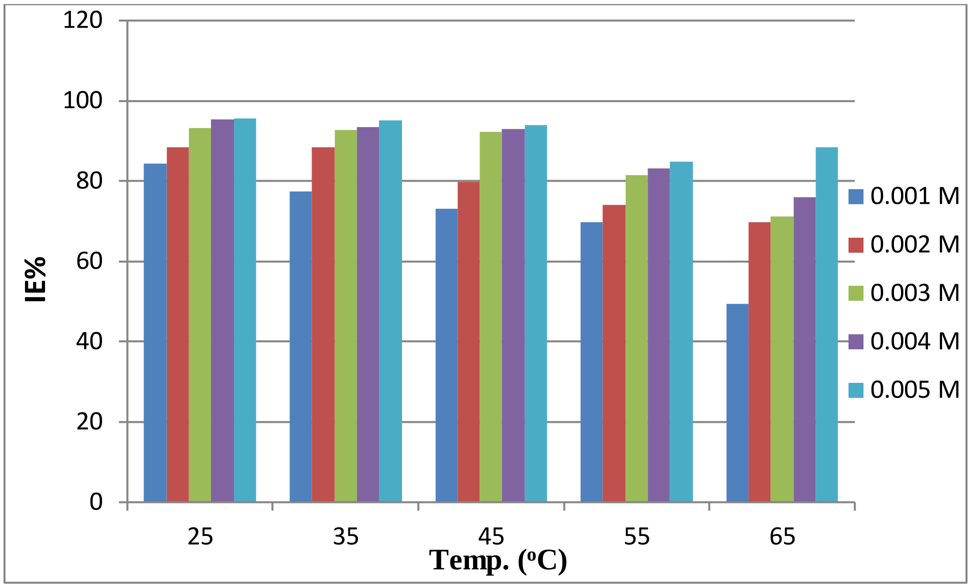

Figure 6: Inhibition Efficiency for different temperatures at varied ABCP concentrations.

3.5. Scanning Electron Microscopy (SEM)

Figure 7. depicts a micrograph of the surface of the coupon showing that the surface was corrosive and rough with a corrosion solution that had no inhibitor of corrosion. The area was rough and rusted. On the metal surface have wrought hydrochloric acid. Due to the creation of a protective surface layer in figure 8, the metal surface was not greatly harmed by corrosion. This shows that the newer manufactured inhibitor prevents corrosion on a metal surface at a temperature of 0.5 M HCl.

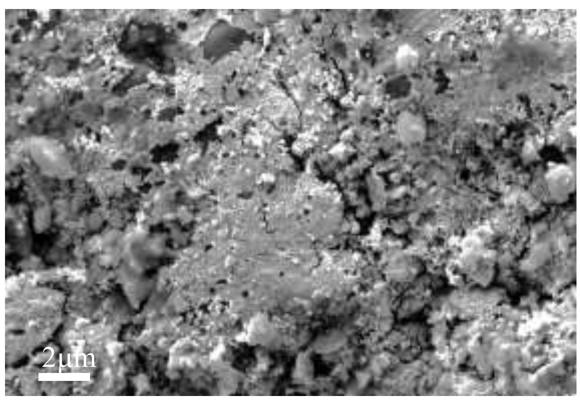

Figure 7: The SEM micrograph in the absence of the corrosion inhibitor for mild steel (ABCP).

3.6. Inhibitive Mechanism

The inhibitor of corrosion may be adsorbed onto a mild steel surface and create an inhibitor to reduce corrosion and increase corrosion impedance in mild steel [18]. There are generally three sorts of mechanisms of inhibition:

1. The method of chemical absorption where the inhibitor molecules adsorb the metal surface and form a protective layer.

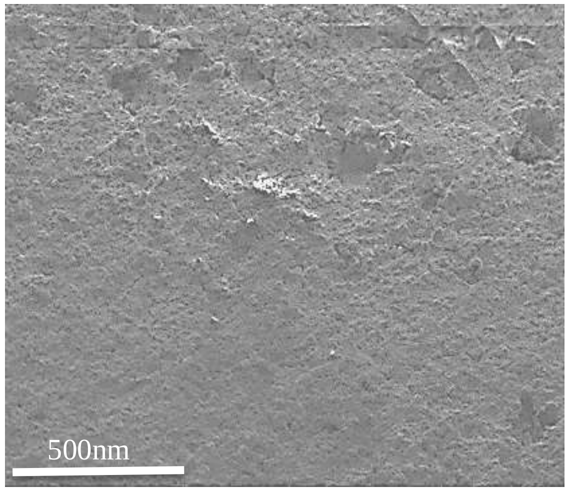

Figure 8: The SEM micrograph in the presence of the corrosion inhibitor for mild steel (ABCP).

2. By defending the base metal, the inhibitor molecules construct a protective coating.

3. When contact with potentially corrosive substances in the environment the inhibitor molecules form metal-complexes [19]. ABCP's mechanistic adsorption of ABCP molecules into a mild steel surface is a first step in the HCl solution as corrosion inhibitor. The development of donor acceptor surface complexes among unshared and/or π electrons from inhibitor molecules were anticipated in prior studies and the empty iron orbital [20].

The number of adsorbent sites, size of molecules, the interaction of the inhibitor and manner of metal surface may all be explained in ABCP molecules against MS corrosion in o.5 M HCl, and the evolution of an insoluble complex. Figure 9 illustrates the unparalleled electrons as well as the double bonds on nitrogen and oxygen atoms formed by metallic-surface chemical bonding.

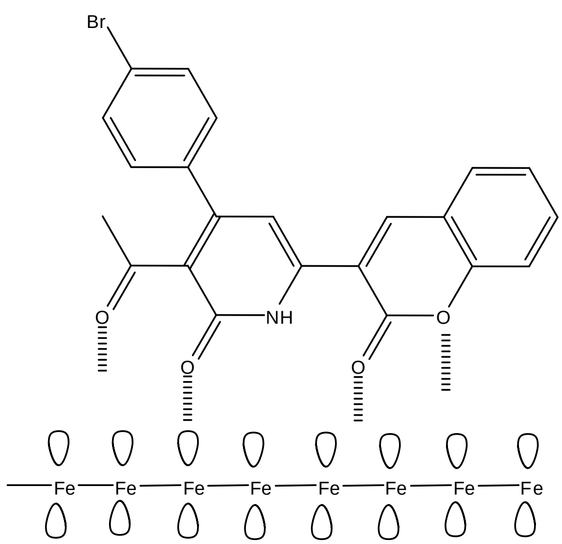

Figure 9: The suggested action on corrosion inhibitor of the ABCP molecule mechanism.

4. Conclusions

The findings of this research revealed that the new pyridine derivative namely compounds 3-acetyl-4-(4-bromophenyl)-6-(2-oxo-2H-chromene-3-yl)pyridine-2(1H)-one (ABCP) in a concentration-dependent approach, it worked as a good corrosion inhibitor for the surface of mild steel in hydrochloric acid solution.IE of ABCP as corrosion inhibitor with superior inhibition efficiency of 98.4% at the concentration of 0.005M decreases with an increasing temperature, which proposed of physisorption. Due to the inclusion of nitrogen and oxygen atoms, ABCP molecules have been shown to be superior inhibitors with good inhibitive qualities. SEM measurements confirming the formation of a protective layer on the coupon surface by inhibitor molecules. The anti-corrosion investigation of compound ABCP molecules clearly indicated its involvement in coupon surface protection in corrosive environments.

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Conflict of Interest
The authors declare no conflicts of interest.

References
[1] M. Faiz, A. Zahari, K. Awang, and H. Hussin, "Corrosion inhibition on mild steel in 1 M HCl solution by: Cryptocarya nigra extracts and three of its constituents (alkaloids)," *RSC Advances*, vol. 10, pp. 6547–6562, 2020.
[2] N. B. I. Akens Hamilton-Amachree, "Corrosion inhibition of API 5L X80 pipeline steel in acidic environment using aqueous extract of Thevetia peruviana," *Chemistry International*, vol. 6, pp. 117–128, 2019.
[3] N. N. Hazani, N. N. Dzulkifli, S. A. I. S. M. Ghazali, Y. Mohd, Y. Farina, and F. Ngatiman, "Synthesis , Characterisation , Crystal Structure and Anti-corrosion Studies of an Organotin (IV) Complex of 2-acetylpyridine 4-ethyl-3- thiosemicarbazone (LH): n-BuSn (L) Cl 2," *ASM Science Journal*, 2019.
[4] M. Khattabi *et al.*, "Performance and computational studies of two soluble pyran derivatives as corrosion inhibitors for mild steel in HCl," *Journal of Molecular Structure*, vol. 1196, pp. 231–244, 2019.
[5] S. B. Al-Baghdadi, A. Kadhim, G. Sulaiman, A. A. Al-Amiery, H. K. Abdul Amir, and M. Takriff, "Anticorrosion and antibacterial effects of new Schiff base derived from hydrazine," *Journal of Physics: Conference Series*, vol. 1795, p. 012021, 2021.
[6] A. Zaher, A. Chaouiki, R. Salghi, A. Boukhraz, B. Bourkhiss, and M. Ouhssine, "Inhibition of Mild Steel Corrosion in 1M Hydrochloric Medium by the Methanolic Extract of Ammi visnaga L. Lam Seeds," *International Journal of Corrosion*, vol. 2020 , p. 10 , 2020.
[7] S. K. Ahmed, W. B. Ali, and A. A. Khadom, "Synthesis and investigations of heterocyclic compounds as corrosion inhibitors for mild steel in hydrochloric acid," *International Journal of Industrial Chemistry*, vol. 10, pp. 159–173, 2019.
[8] H. Wei, B. Heidarshenas, L. Zhou, G. Hussain, Q. Li, and K. (Ken) Ostrikov, "Green inhibitors for steel corrosion in acidic environment: state of art," *Materials Today Sustainability*, vol. 10, p. 100044, 2020.
[9] N. Kumar, "Synthesis of 3-substituted phenyl-1-(3- coumaryl)propan-1-one derivatives using secondary amine catalysts, " word Research J. of Bio, vol.1, pp.20-26, 2012.
[10] H. H. Ibraheem, "Synthesis and Microbiological Investigation of Progesterone Derivatives," *Engineering and Technology Journal*, vol. 31, pp. 687–697, 2013.
[11] Y. F. Mustafa, "Synthesis, characterization and antibacterial activity of novel heterocycle, coumacine, and two of its derivatives," *Saudi Pharmaceutical Journal*, vol. 26, pp. 870–875, 2018.
[12] H. Ibraheem, L. Sami, and Y. K. Al-majedy, "Synthesis and Characterization of New Complexes Derived from 4- (4- (Dimethylamino) Phenyl) -2-Oxo- Dihydropyridine -3-Carbonitrile with Manganese (II), Iron (II), Cobalt (II), and Nickel (II) Ions," *Scientific Conference on Environment and Sustainable Development (3rd : 2017 : Baghdad, Iraq)*, vol. 36, pp. 184–191, 2018.
[13] E. Berdimurodov, A. Kholikov, K. Akbarov, and G. Xu, "dithione for carbon steel in 1 M HCl

medium : gravimetric , electrochemical , surface and quantum chemical analyses," *Arabian Journal of Chemistry*, vol. 13, pp. 7504–7523, 2020.

[14] M. A. Abdallah, S. M. Gomha, I. M. Abbas, M. S. H. Kazem, S. S. Alterary, and Y. N. Mabkhot, "An efficient synthesis of novel pyrazole-based heterocycles as potential antitumor agents," *Applied Sciences (Switzerland)*, vol. 7, 2017.

[15] Q. A. Jawad *et al.*, "Potential of Novel Thiosemicarbazone on Mild Steel in Sulfuric Acid Environment," *Coatings*, vol. 9, pp. 729, 2019.

[16] A. Al-amiery, L. M. Shaker, A. A. H. Kadhum, and M. S. Takriff, "Synthesis, characterization and gravimetric studies of novel triazole-based compound," *nternational Journal of Low-Carbon Technologies*, vol. 15, pp. 164–170, 2020.

[17] H. Acid *et al.*, "Evaluation of 2-Mercaptobenzimidazole Derivatives as Corrosion Inhibitors for Mild Steel in," *Metals*, vol. 10, pp. 1–14, 1995.

[18] ASTM G1-03(2017)e1, "Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens," *ASTM International, West Conshohocken, PA*, 2017.

[19] H. Ju, Z.-P. Kai, and Y. Li, "Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: A quantum chemical calculation," *Corrosion Science*, vol. 50, pp. 865–871, 2008, doi: 10.1016/j.corsci.2007.10.009.

[20] H. R. Obayes, A. A. Al-Amiery, G. H. Alwan, T. A. Abdullah, A. A. H. Kadhum, and A. B. Mohamad, "Sulphonamides as corrosion inhibitor: Experimental and DFT studies," *Journal of Molecular Structure*, vol. 1138, pp. 27–34, 2017.