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Eco-Friendly Synthesis of Heterocyclic Compounds and Evaluation of Their Corrosion Inhibition Activities for Mild Steel in 1N Sulfuric Acid

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ABSTRACT

This study explores the green synthesis, characterization, and corrosion inhibition properties of two novel heterocyclic compounds, 8-((2-(3-hydroxybenzyl) hydrazineyl)methyl)-4-methyl-2H-chromen-7-ol (HHMC) and 7-(3-hydroxybenzyl)-4-methyl-8,9-dihydropyrano[2,3-e]indazol-2(7H)-one (HBPI). HHMC was synthesized via microwave-assisted reaction while HBPI by cyclization and characterized using elemental analysis, IR, H^1 NMR, and C^{13} NMR spectroscopy. The corrosion inhibition efficiencies of HHMC and HBPI for mild steel in 1N H_2SO_4 were evaluated using weight loss measurements, scanning electron microscopy (SEM), and potentiostatic polarization techniques. Weight loss studies revealed that both inhibitors significantly reduced corrosion rates, with HBPI demonstrating superior inhibition efficiency. SEM analysis confirmed the formation of protective films on the steel surface, with HBPI forming a more robust and effective layer. Polarization studies indicated that both compounds acted as mixed-type inhibitors, suppressing cathodic and anodic reactions, with inhibition efficiency improving with increasing inhibitor concentration.

Keywords: *Green synthesis, Heterocyclic compounds, Corrosion Inhibition Efficiencies*

Introduction

Industries including petroleum, fertilizers, and polymers are currently facing serious corrosion-related issues, and they are continuously in need of improved, more reasonably priced, and ecologically friendly corrosion inhibitors or formulations to deal with these issues (Quraishi, 2020; Yadav, S. 2016). Traditional corrosion inhibitors are excellent at preventing corrosion, but due to their toxicity or manufacturing methods, they are not environmentally benign (Yadav, S. 2016). As a result, there has been a growing focus on replacing synthetic, non-environmentally benign inhibitors with competent, "green" created inhibitors that are efficient and produced utilizing eco-friendly methods (Khan, A 2022,Yadav, S. 2023). Imidazole, triazole, pyridine, pyrazole, quinoline, tetrazole, pyrimidine, purine, and pyrrole are examples of heterocyclic organic compounds having anti-corrosive properties that have nitrogen as their primary heteroatom. Other heteroatoms including S, O, and nitrogen-containing rings also contribute to the formation of protective coatings on metal surfaces by complexation and adsorption processes, which reduces the rates of oxidation and corrosion. These heterocycles' unique electronic structures and potent interactions with metal atoms, enabled by their N, S, and O donor sites, make them effective corrosion inhibitors in a range of industrial applications (Yadav, 2024; Yadav, 2023; Yadav, 2021, 2022, 2021). This study examines novel heterocyclic compounds' ecologically friendly synthesis, characterization, and corrosion-prevention properties on mild steel in 1N H_2SO_4. This study uses scanning electron microscopy (SEM), potentiostatic polarization, and weight loss measures to assess the inhibitory effectiveness of two synthesized compounds, HHMC and HBPI. This work aims to evaluate the potential of these novel heterocyclic compounds as corrosion inhibitors using both theoretical and experimental approaches in order to help develop safer and more sustainable corrosion control technologies.

Material and Methods

All of the chemicals were purchased from Sigma Aldrich and used without any sort of purification or processing.

Test specimen: Composition of mild steel: C = 0.13, Mn = 0.37, Si = 0.16, S = 0.025, P = 0.03, Fe = 99.28

Acid solution for corrosion test: Analytical grade $H_2SO_4$was diluted with distilled deionized water to create solutions with a 1N concentration. To completely dissolve the inhibitors, two to three milliliters of 100% ethanol were utilized.

Evaluation of corrosion inhibition efficiencies: The potentiostatic polarization technique, the weight loss method, and scanning electron microscopy (SEM) were used to assess the corrosion inhibition efficacy of the produced inhibitors.

Synthesis of 8-((2-(3-hydroxybenzyl) hydrazineyl) methyl)-4-methyl-2H-chromen-7-ol (HHMC): 1.762 grams7-hydroxy-4-methyl coumarin (0.01 moles) and 1.38 g (0.01 moles) of 3-(hydrazineylmethyl) phenol dissolved in 50 ml of ethanol, 7.1 ml of formaldehyde was added, and the mixture was microwave-irradiated for approximately 30 minutes (300W) (Yadav and Chauhan, 2024). Finally 50 m lof water and 100 grams of crushed ice are added to the reaction mixture that resulted solid product is filtered, washed, and recrystallized by hot ethanol. 80% was the percentage yield.

Characterization of compound HHMC

Characteristic I.R. bands (KBr disc): 3370.10cm^{-1}, 3213cm^{-1} (OH str.) 3015 cm^{-1} (NH), 2980 CH str.), 1680 cm^{1}, 1645 cm^{-1},1522 cm^{-1}, 1374cm^{-1} (C=O,C=C,.) 1253 cm^{-1}, 1212cm^{-1}, 1115 cm^{-1}, 747 cm^{-1}

H^1NMR: (300 MHz, DMSOd6, TMS, delta, ppm**):** 10.09 (NH-CO),9.66 (OH) 8.21 (CH) 8.12(CH) 7.51(CH), 7.51(CH), 6.67(CH)6.28(COCH) 5.01(NH), 4.00(CH_2), 2.50(CH_3), 2.41(CH3)

C^{13}HNMR:(62.5MHz, DMSOd6, TMS,ppm): 160.7, 156.8, 153.5, 152.7, 149.7, 143.1, 129.8,124.3, 121.2, 119.4,119.0, 113.8, 112.5, 112.4, 111.8, 55.6, 43.5. 19.4

Synthesis of 7-(3-hydroxybenzyl)-4-methyl-8,9-dihydropyrano [2,3-e]indazol-2(7H)-one (HBPI): 0.1 M of **8**-((2-(3-hydroxybenzyl) hydrazineyl) methyl)-4-methyl-2H-chromen-7-ol was shocked in Con.H_2S0_4 and leaved for 2 hours and a light grey colour was appeared and resultant reaction mixture was filtered and washed and recrystallized by using hot ethanol water mixture 80:20,. % yield= 80%.

Characterization of compound HBPI

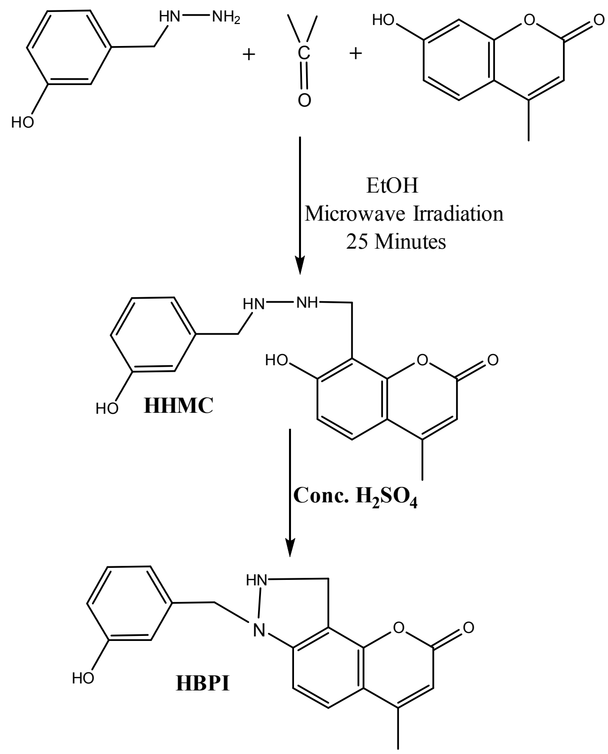
Characteristic I.R. bands (KBr disc): 3467.10 cm^{-1}, 3316 cm^{-1} (OH str.) 3050cm^{-1} (NH), 2975 cm-1CH str.), 1687cm^{1}, 1655 cm^{-1}, 1542 cm^{-1}, 1372cm^{-1} (C=O,C=C,.)1250 cm^{-1}, 12241m^{-1}, 1121cm^{-1}, 787 cm^{-1}

H^1NMR: (300 MHz, DMSOd6, TMS, delta, ppm**):**

Chemical formula	M.P.	Colour	Molecular Mass	Elemental Analysis Observed (Calculated)
$C_{18}H_{20}N_2O_3$	152^{oC}	Cream White	312.37	C= 69.11 (69.21); H= 6.44 (6.45); N= 8.60 (8.97); O= 15.21 (15.37)

Chemical formula	M.P.	Colour	Molecular Mass	Elemental Analysis Observed(Calculated)
$C_{18}H_{16}N_2O_3$	168	Light grey	308	C= 70.11 (70.12) ; H= 5.14 (5.23); N= 9.20 (9.09); O= 15.49 (15.57)

9.29 (OH) 6.82, 6.91, 7.08, 8.86, (CH- Phenyl), 6.85, 7.45, 6.25(CH-Chromone), 4.7(NH), 4.32(CH_2), 3.90(CH_2-NH), 2.43(CH_3) **C^{13}** **HNMR:** (62.5MHz, DMSOd6, TMS,ppm): 160.6, 156.7, 152.5, 149.7, 142.7, 143.1, 129.8,122.3, 119.2, 118.4, 113.8,112.8, 112.4, 109.8,109.6, 66.2, 51.1. 19.4



Scheme 1. Microwave Synthesis of HHMC & HBPI

Results and Discussion

The following techniques were used to assess the effectiveness of corrosion inhibition

Weight loss Methods: These methods evaluate the inhibition efficiency (IE (%)) of inhibitors in an acidic corrosive medium (1N H_2SO_4) by comparing weight loss with and without inhibitors

HHMC & HBPI. Inhibition efficiencies can be calculated using Equation 1.

IE (%) Inhibition Efficiency = (W0-WI /W0) × 100 .. (1)

Weight loss without inhibitors is denoted by W0, while weight loss with inhibitors is denoted by WI. Fig. 1 provide visual representations of the corrosion rate and inhibition efficiencies.

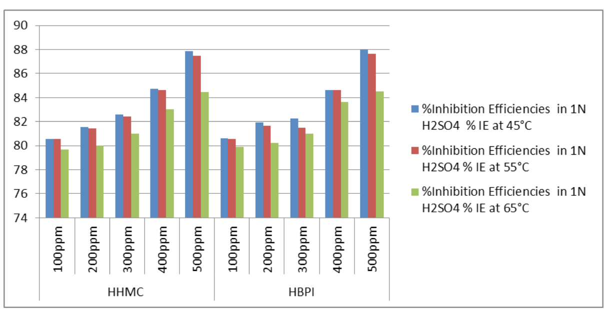


Fig. 1. Inhibition efficiencies of HHMC & HBPI

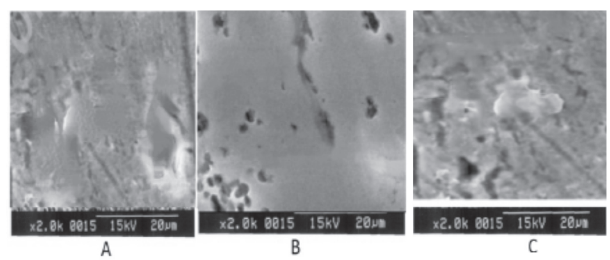


Fig. 2. The SEM results given in the figure of corrosion inhibitior compound HHMC & HBPI. Image A represents results when mild steel sample dipped in solution of HBPI+ 1N H2SO4, Image B represents results when mild steel sample dipped in solution of only in 1N H2SO4 and image C represents results when mild steel sample dipped in solution of HHMC+ 1N H2SO4

Scanning Electron Microscopy (SEM)

The surface appears in (A) smoother and relatively intact compared to the other images. Some minor irregularities or deposits might be visible, which could indicate the formation of a protective film by HBPI on the steel surface. There is no significant evidence of deep pits or widespread corrosion.

HBPI acts as an effective corrosion inhibitor, likely forming a strong adsorbed layer on the steel surface. This layer protects the metal by reducing the interaction between the acid and the substrate, minimizing the corrosion process. HBPI demonstrates strong corrosion inhibition properties.

The surface is heavily corroded in (B), showing deep pits and rough morphology. The presence of corrosion products and severe surface degradation is evident. In the absence of any inhibitor, the mild steel is fully exposed to the corrosive environment of 1N HSO. The aggressive ions lead to metal dissolution and the formation of surface defects This image serves as the control, highlighting the extent of corrosion in the absence of protection.

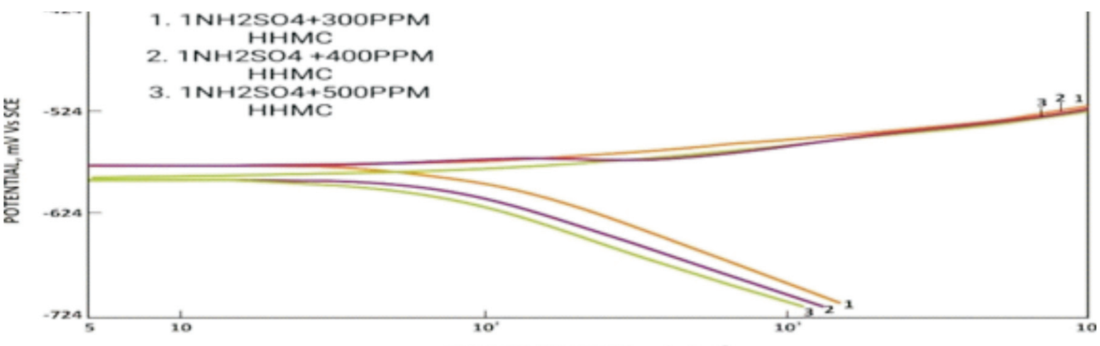
The surface is less rough than Image B in image (C) but shows some localized damage or pits. The protection is evident, but not as significant as in Image A, as some signs of corrosion are still visible. HHMC provides moderate inhibition by forming a protective film on the steel surface, but it may not be as effective as HBPI. The observed pits suggest that HHMC adsorption or interaction with the steel surface may be less robust compared to HBPI. HHMC reduces corrosion to some extent but does not perform as well as HBPI.

Potentiostatic Polarization Technique

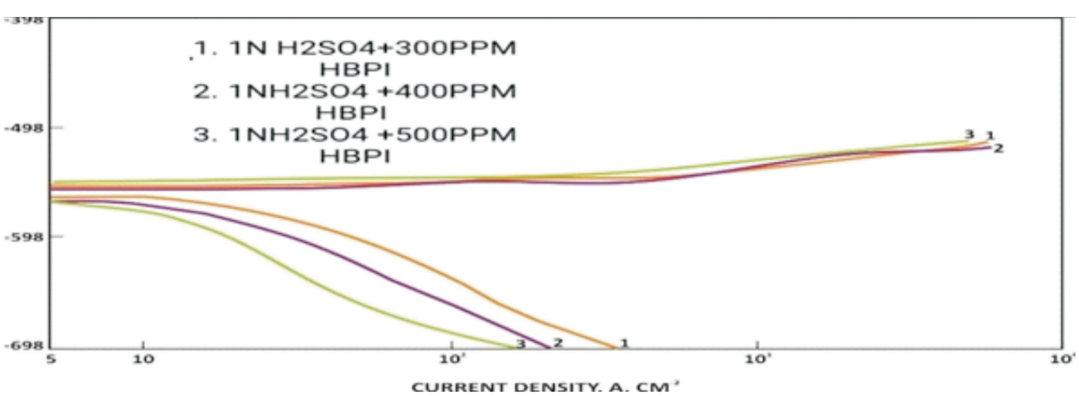
The figure 2 (A) (B) represent the potentiostatic polarization analysis of two corrosion inhibitor compounds, HHMC (first figure) and HBPI (second figure), in 1N H2SO solutions with different concentrations (300 ppm, 400 ppm, and 500 ppm). For both HHMC and HBPI, an increase in the inhibitor concentration (from 300 ppm to 500 ppm) results in a shift of the curves, indicating an improvement in the inhibition efficiency. This is characterized by a decrease in the cathodic and anodic current densities, suggesting that both inhibitors effectively reduce the corrosion rate by suppressing both anodic and cathodic reactions. Both inhibitors show similar trends, but the polarization curves for HBPI (Figure B) are more stable, suggesting that HBPI may provide slightly better or more consistent corrosion protection than HHMC under the same conditions. The polarization analysis reveals that both HHMC and HBPI are effective corrosion inhibitors in 1N H2SO4H_2SO_4H2SO4, with their efficiency improving as the concentration increases. HBPI demonstrates slightly better inhibition performance compared to HHMC, particularly at higher concentrations.

Conclusion

This study successfully synthesized and characterized two novel corrosion inhibitors, HHMC and HBPI, using microwave-assisted synthesis. Comprehensive methods, including weight loss techniques, SEM, and potentiostatic polarization, were employed to evaluate their corrosion inhibition efficiencies in a 1N HSO medium. HHMC and HBPI were synthesized with high yields (80%) and character-



(A) Potentiostatic polarization analysis results of HHMC



(B) Potentiostatic polarization analysis results of HBPI

Fig. 2. Potentiostatic polarization analysis of two corrosion inhibitor compounds, HHMC (A) and HBPI (B), in 1N H_2SO_4

ized using elemental analysis, IR, H^1 NMR, and C^{13} NMR. Both compounds displayed well-defined physical and spectral properties, confirming their molecular structures and purity.Weight loss studies indicated that both inhibitors significantly reduced the corrosion rate of mild steel in acidic conditions, with HBPI showing superior performance compared to HHMC. SEM analysis revealed the formation of protective films on the steel surface, which were more robust for HBPI, effectively minimizing surface damage and pit formation. Polarization studies demonstrated that both inhibitors suppressed cathodic and anodic reactions, with inhibition efficiency improving as inhibitor concentration increased. HBPI exhibited slightly better inhibition performance, particularly at higher concentrations (500 ppm). The observed inhibition behavior suggests that both HHMC and HBPI adsorb onto the steel surface, forming a protective layer that reduces metal dissolution and interaction with aggressive ions in the acidic environment. The enhanced efficiency of HBPI can be attributed to its stronger adsorption and more stable protective film formation compared to HHMC.

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