Characterization and inhibition efficiency of HCAE as a corrosion inhibitor in saline and acidic environments

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Article

ABSTRACT

In this work, we synthesized (E)-2-hydroxyethyl 3-(4-oxo-4H-chromen-3-yl) acrylate (HCAE). ^{1}H-NMR and ^{13}C-NMR spectroscopy was used to characterize the compound. We examined the HCAE's anticorrosion characteristics at 100, 200, and 300 ppm concentrations in two distinct mediums, 3.5% NaCl and 1M HCl. Electrochemical spectroscopy (EIS) findings at 303K revealed that the HCAE inhibitor achieved 88.89% protection effectiveness in 1M HCl and 93.88% protection efficiency in 3.5% NaCl, demonstrating exceptional inhibition efficiency at 300 ppm. Furthermore, the

HCAE

efficacy of the HCAE in preventing corrosion was investigated through Scanning Electron Microscopy (SEM) to analyze the structural morphology of the protective layer that developed on the mild steel surface.
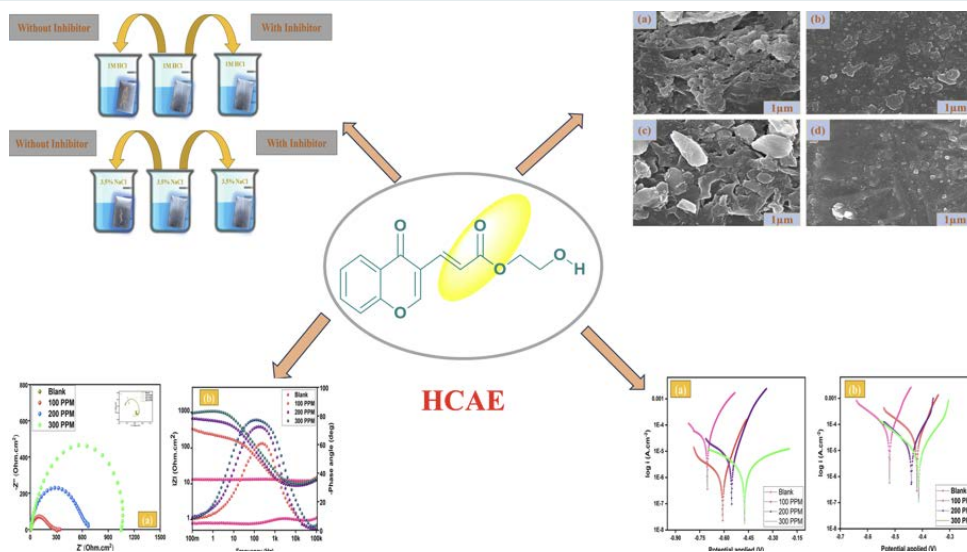
Keywords: 3-Substituted chromone derivatives; Low alloy steel; Corrosion inhibitor; Electrochemical spectroscopy; FE-SEM

INTRODUCTION

Mild steel (MS) alloy is widely used in industrial and construction processes because, among other things, it is affordable, easily accessible, and has a high mechanical strength. But because of its extreme susceptibility to corrosive media, it suffers disastrous financial losses, including unplanned manufacturing unit shutdowns.[1] In many sectors, preventing corrosion in carbon steel structures remains the top priority. When protecting mild steel alloy against corrosion, corrosion inhibitors are one of the most used techniques,[2] particularly in harsh environmental conditions.[3,4] Since hydrochloric acid (HCl) and sodium chloride (NaCl) are often encountered as corrosive substances, they are perfect choices for our investigation.[5]

A corrosion inhibitor's molecular structure is a key component of its corrosion prevention technique. The literature suggests that the interactions of organic molecules containing heteroatoms, which include oxygen, nitrogen, sulfur, and phosphorus, with metal surfaces result in promising inhibitory efficiency.[6–8] Environmental risks are associated with corrosion inhibitors because of their toxicity and expensive production methods. Drug molecules are being used as effective anticorrosive materials by scientists to create environmentally acceptable organic inhibitors using non-toxic reagents.[9] Chromones (4H-Chromene-4-ones) are heterocyclic molecules having numerous physiological impacts, including those that are neuroprotective, anti-HIV, anti-bacterial, anti-cancer, and anti-allergic, are widely recognized.[10,11]

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The chromone's reactivity and capacity to interact with biological molecules are increased by the addition of an acrylic ester group at its 3-position, which may help to produce antibacterial properties.[11] The capacity of chromones to form stable chelates with metal ions and their bioactive characteristics are well recognized. Reactive double bonds are introduced by the acrylic acid molecule, which may help polymerization or contact with metal surfaces. These compounds are especially noteworthy for corrosion research since they are powerful compounds that form coordination complexes due to their remarkable ability to donate electrons to metal ions.[12]

Although ethylene glycol and its derivatives are hygroscopic and can create a protective layer on metal surfaces, they are frequently utilized in corrosion inhibitors.[13] The synergistic action of ethylene glycol, and chromone-3 acrylic acid can improve overall anti-corrosive capabilities. The efficiency of the protective layer can be increased by the ester linkage and aromatic chromone structure, which can offer good adherence to the metal surface. In this work, we used dicyclohexylcarbodiimide (DCC)[14,15] as the coupling agent to synthesize (E)-2-hydroxyethyl 3-(4-oxo-4H-chromen-3-yl) acrylate (HCAE). The main objective is to examine this synthesized compound's ability to resist corrosion in acidic and neutral medium at different concentrations (100 ppm, 200 ppm, and 300 ppm). Examining the HCAE in 1M HCl and 3.5% NaCl is because, in practical applications, metals and alloys are subjected to a range of corrosive conditions. This ensures the compound's practical effectiveness and reliability. The study emphasizes how effective the synthesized compound can be as a corrosion inhibitor in saline and acidic environments

EXPERIMENTAL

Material and Methods

The organic solvents and all the chemicals were bought from Merck Sigma Aldrich; however, the solvents were dried and distilled before use. Thin-layer chromatography (TLC) was used to monitor each reaction. ^1H & ^{13}C NMR were recorded on JEOL ECZ-500 R spectrophotometer in $CDCl_3$ solvent. The coupling constant (Hz) and chemical shift (δ) are expressed in ppm relative to TMS. Low alloy steel (LAS) sheets used were composed of remaining iron (Fe), C = 0.06, Si = 0.08, Mn = 0.36, S = 0.010, P = 0.013, Ni = 0.01, Cu = 0.01, and Cr = 0.01. The elemental composition data was given by the Shriram Institute of Industrial Research, Delhi, India, utilizing SRI/CHE-MET/15, IS:228(Pt-1, Pt-3)1987, and IS:228(Pt-8, Pt-9)1989 standard protocols. Grades 200, 400, 800, and 1200 emery paper were utilized to polish and abrade the plate surface. The electrochemical studies were performed using Autolab potentiostat PGSTAT204 equipped with a traditional three-electrode system. Morphological studies were done by using a ZEISS EVO 18 SEM at the 1µM resolution recorded following exposure to both 1 M HCl and 3.5% NaCl for 24 hours, both with and without inhibitors.

Procedure for the synthesis of HCAE

The chromone 3- acrylic acid used in the synthesis of HCAE was prepared by a mixture of 3.5 g (20 mmol) of 3-formyl chromone and 2 g (20) mmol of malonic acid, together with 20 mL of pyridine, was refluxed in a 100 mL round-bottom flask for 30 to 45 minutes while stirring constantly. The reaction mass was allowed to cool to

ambient temperature, the pH was brought to 1.0 using concentrated HCl, and the reaction mixture was agitated for half an hour. The resulting yellow-coloured product was filtered, cleaned with cold 1N HCl, and allowed to dry.[16]
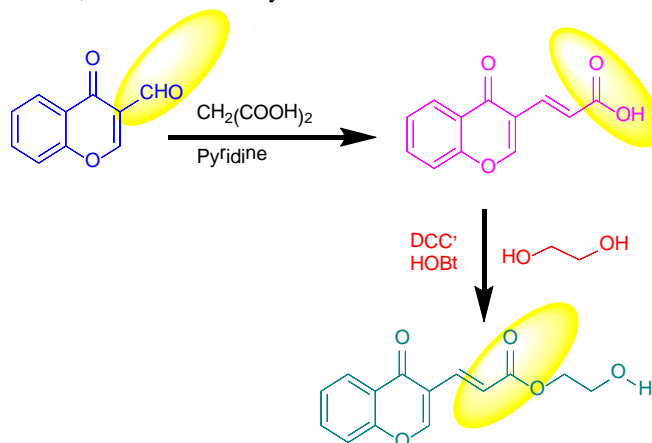
Scheme 1. Synthetic route of HCAE

A solution of Chromone-3-acrylic acid (3.0 mmol) in dimethylformamide (10 mL) was supplemented with 8.0 mmol of HOBt, and 8.0 mmol of DCC. The reaction mixture was then stirred overnight at room temperature after the amount of required ethylene glycol (3.5 mmol) was added. After the reaction was completed, the mixture was cooled to 0°C before being filtered. The reaction's progress was observed using TLC. The filtrate was evaporated, and then 10 mL of methylene chloride was added to the solid to take out any residual dicyclohexylurea[14]. After the methylene chloride layer was vaporized, the crude product that was left over was further purified using column chromatography and ethyl acetate/petroleum ether with a 2:8 ratio to produce the required ester in a yield of 70-72 %.

(E)-2-hydroxyethyl 3-(4-oxo-4H-chromen-3-yl) acrylate: white solid; yield 70-72%; melting point 92°C.

1H-NMR data (CDCl3,500MHz): δ 3.38 (t, 2H),3.6 (s, -OH), 4.05 (t, 2H, -OCH2),7.39(d, 2H, J=16.0 Hz, H-2') 7.65-7.58 (m, 3H, H-1' H-6, H-8), 7.86 (t,1H, J=8.9Hz, H-7), 7.89 (s, 1H, H-2) and 8.19 (d,1H, J=8.0Hz, H-5). 13C-NMR data (CDCl3, 500MHz): δ 47.93,54.94, 116.26 117.63, 122.15, 122.41,123.94, 124.50, 132.11, 132.78, 153.56, 156.31, 166.50 and 174.21.

Electrochemical Measurements

An electrode that was functional or operational in the electrochemical cell had a 1 cm² opening to the electrolytic solution. Using 1.0 mV/s as a scanning rate, a potential window spanning from -250 mV to +250 mV was employed for the potentiodynamic polarisation investigation. The acquisition of data for Electrochemical Impedance Spectroscopy was performed using an amplitude of 10 mV ac signal, spanning from 100 kHz to 0.01 Hz. Max frequency (f_{max}), and charge transfer resistance (R_{ct}) are examples of EIS parameters. Double layer capacitance (C_{dl}) and inhibitory efficiency (%) were computed by the following relation based on EIS data.[17]

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (1)$$

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$$\% \text{ Protection efficiency}(\eta) = 1 - \frac{C_{dl}(MS)}{C_{dl}\,(epoxy)} \times 100 \quad (2)$$

$$\% \text{ Protection efficiency}(\eta) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$

RESULT AND DISCUSSION

### Chemistry and Weight Loss Analysis

The inhibitor compound i.e. chromone-ester (HCAE) was synthesized by a process involving two stages that were carried out per the literature procedure.[14] In the first stage, chromone 3- acrylic acid was yielded by Knoevenagel condensation with malonic acid. In the next stage, we synthesized HCAE by coupling chromone 3-acrylic acid with ethylene glycol in the presence of 1-hydroxy benzotriazole (HOBt) and dicyclohexyl carbodiimide (DCC) (Scheme 1). In ^{1}H-NMR two distinct triplets at 4.052 and 3.381ppm, attributed to ester linkage (-OCH$_2$) and a broad singlet at 3.68 for OH. The rest are for the aromatic ring and α, β-unsaturation (8.19-7.16). In ^{13}C-NMR spectra for HCAE, the characteristics peaks of -OCH$_2$ and C=O of ester are at 54.94, 47.93, and 166.50 ppm respectively. The peak at 174.21 is for pyran C and the rest are for aromatic ring C and α, β-unsaturated C. Both NMR pictures are given in supplementary information.
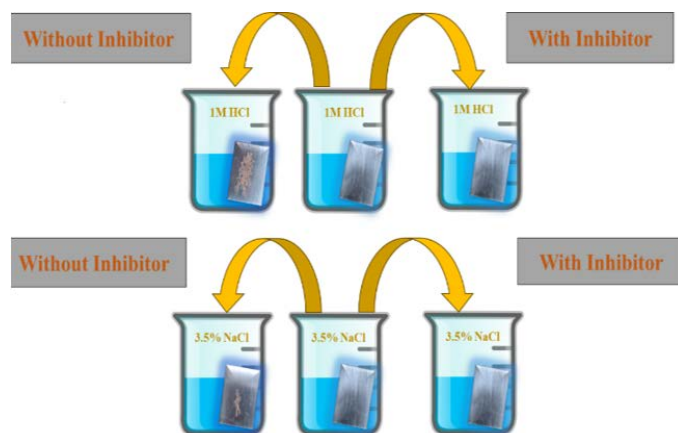
Figure 1. Illustration displaying the weight loss study in a medium containing 3.5% NaCl and 1M HCl solution

We used a weight loss study, as illustrated in Figure 1, to evaluate the corrosion-restrictive performance of MS alloy at various concentrations of HCAE in a 1 M HCl solution and a 3.5% NaCl solution. To assess the persistence of inhibitive behavior, the impact of submerged periods on HCAE inhibition efficacy was also examined at different immersion time intervals up to 144 h in both media as shown in Figure 2[18].

HCAE has shown effective mild steel corrosion inhibitor at all concentrations with notable impact at higher concentrations In both mediums, HCAE reached its maximum inhibitory effectiveness value of 88.89 % (HCl) and 93.88% (NaCl) at 300 ppm. The adsorption capabilities of electron-rich aromatic rings, ester linkage, and oxygen moieties seem responsible for HCAE's excellent effectiveness as a corrosion inhibitor.
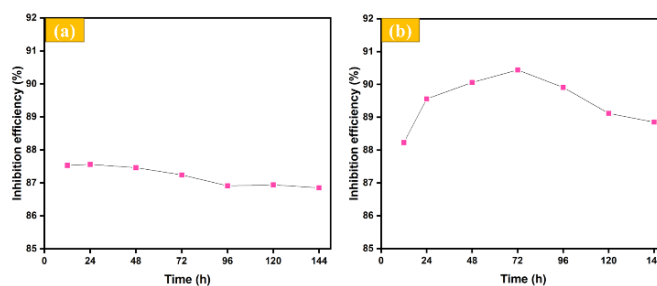
Figure 2. (a) Effect of the submerged period on HCAE's inhibition efficiency (%) in 1M HCl; (b)Effect of the submerged period on HCAE's inhibition efficiency (%) in 3.5% NaCl at 303 K.

EIS measurement

A more comprehensive mechanistic understanding of the interaction modes i.e., charge transfer, adsorption, and diffusion, and at the mild steel surface during the electrochemical process is provided by the EIS tests carried out in both inhibited and uninhibited solutions. Figure 3 and Figure 4 display the Nyquist and Bode forms of the experimental data from the EIS investigation for 1M HCl and 3.5% NaCl. The semicircle loops in our data have a little depression in comparison to the theoretically obtained Nyquist plots. This typical behavior of the inadequate capacitance loop is related to the mild steel electrode's variability, frequency dispersion, and hardness. Additionally, the capacitive loop's width significantly increases with the addition of the inhibited solution, and at higher concentrations, the loop becomes notably more apparent. These findings indicate that the presence of the inhibitor molecules changed the metal-solution interface.
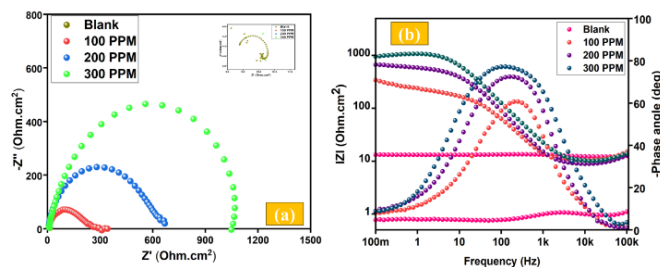
Figure 3. (a) Nyquist diagram for mild steel(MS) specimen in 1M HCl at different HCAE concentrations; (b) Bode diagram for mild steel(MS) specimen in 1 M HCl solution at varying HCAE inhibitor concentrations

On comparing Figure 3 (a) and Figure 4 (a), it is very evident that when the concentration of the HCAE is increased from 100 ppm to 300 ppm, then the R$_{ct}$ value increases significantly in both media. The inhibitor's impact is more pronounced in the NaCl medium, as evidenced by the higher Rct value (1346.33 Ω) compared to the HCl medium (1058.92 Ω) as shown in Table 1. This might be the result of improved adsorption and the saline environment's ability to produce a more stable protective coating. In the bode plot, as shown in Figures 3(b) and 4 (b), the initial phase angles are relatively low in both media, indicating minimal protection and high corrosion activity on the mild steel alloy surface.

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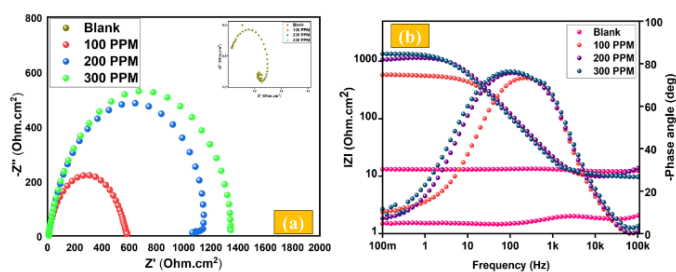
Figure 4. (a) Nyquist diagram for mild steel (MS) specimen in 3.5% NaCl at different HCAE concentrations; (b) Bode diagram for mild steel (MS) specimen in 3.5% NaCl solution at varying HCAE inhibitor concentrations

The phase angle is slightly higher in 3.5% NaCl (10.23°) compared to 1M HCl (8.23°), suggesting that the chloride ions in NaCl provide slightly different corrosion dynamics than the highly aggressive acidic environment of HCl. The phase angle increases dramatically from 8.23° to 77.24° in 1M HCl and from 10.23° to 76.27° in 3.5% NaCl as well. The significant rise in phase angle in both mediums suggests that a protective layer is forming to prevent corrosion on the mild steel surface. The compound appears to be equally effective at altering the electrochemical interface and improving surface protection, as indicated by the nearly same phase angle values at 300 ppm in both mediums. In both plots, the HCAE inhibitor greatly improves corrosion prevention. Significant increases in phase angles signify the development of a protective layer. The impedance values show greater performance in the NaCl environment together with enhanced corrosion resistance. Although the inhibitor works well in both mediums, the greater Z_{max} value in 3.5% NaCl suggests that it provides comparatively superior protection against corrosive processes in a saline environment.

Potentiodynamic polarisation
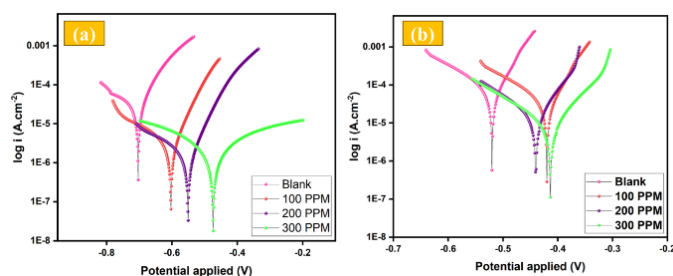
Figure 5. (a) Tafel plot for mild steel (MS) specimen at different HCAE concentrations in 3.5% NaCl; (b) Tafel plot for mild steel (MS) specimen at different HCAE concentrations in 1M HCl

Figure 5 (a) and Figure 5(b) depicted the polarization curve of mild steel(MS) at various concentrations of HCAE in 3.5% NaCl and 1M HCl media respectively after immersion for 24 h in each media. For the NaCl solution without an inhibitor, the corrosion potential (E_{corr}) is even lower than in HCl, suggesting a more noble corrosion process. However, the corrosion current density (i_{corr}) is lower compared to HCl, indicating that NaCl is less aggressive than HCl under these conditions. The addition of inhibitor HCAE from 100 ppm to 300 ppm in both media, further decreases the i_{corr} and shift E_{corr} more positively, enhancing the protective effect as data

given in Table 1. The greater decrease in i_{corr} in comparison to the initial results suggests that the inhibitor is more efficient in NaCl than in 1M HCl. Additionally, the shift in E_{corr} is more noticeable in NaCl, indicating that the inhibitor functions better in less hostile situations.

Table 1: Corrosion parameters derived from electrochemical techniques of mild steel specimen on HCAE at 303 K in 1M HCl and 3.5% NaCl

Inhibitor	C (ppm)	R_{ct} (Ω cm^2)	C_{dl} (μF/ cm^2)	E_{corr} (V)	i_{corr} (μA)	I.E%
1M HCl						
Blank	-	10.23	584	-0.46	111.22	**-**
HCAE	100 ppm	326.78	55.8	-0.43	34.54	**68.94**
HCAE	200 ppm	669.23	34.7	-0.40	16.43	**85.22**
HCAE	300 ppm	1058.92	26.8	-0.37	12.35	**88.89**
3.5% NaCl						
Blank	-	13.20	539	-0.66	82.42	**-**
HCAE	100 ppm	584.13	41.8	-0.60	13.51	**83.6**
HCAE	200 ppm	1142.08	18.9	-0.54	8.11	**90.16**
HCAE	300 ppm	1346.33	11.4	-0.48	5.04	**93.88**

Surface morphology by SEM analysis

Studying the surface topography of mild steel(MS) in a 3.5% NaCl solution and 1M HCl solution after 24 hours both with and without an inhibitor demonstrates that the inhibitor's protective coating has formed.[19] Without inhibitor mild steel surfaces show severe corrosion after 24 hours in 1 M HCl, resulting in pitting, rough surfaces, and degradation. In a 3.5% NaCl solution, the corrosion is less severe due to chloride ions causing localized pitting and crevice corrosion as demonstrated in Figure 6(a) and Figure 6(c).
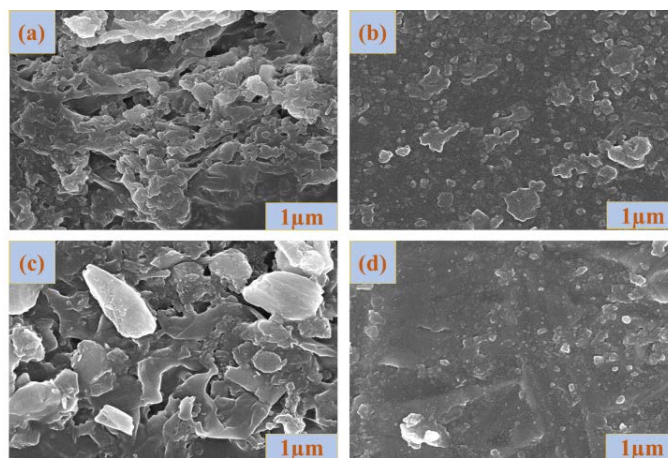
Figure 6. Scanning Electron Micrographs of (a) Blank and (b) HCAE at 303K and 400 ppm in 3.5% NaCl; (c) Blank and (d) HCAE at 303 K and 400 ppm in 1M HCl

After adding HCAE at 300 ppm concentration, both conditions show that the inhibitor is effective, however, the degree of protection may differ. The inhibitor reduces the degree of pitting and surface deterioration in the extremely aggressive 1 M HCl solution. Pitting and crevice corrosion are effectively reduced by

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the inhibitor in the less aggressive 3.5% NaCl solution, leaving a smoother and more uniform surface.[19]

The results obtained validate that the inhibitor considerably decreases corrosion in both the 1 M HCl and 3.5% NaCl mediums by creating an efficient protective film on the mild steel surface. Because the NaCl media is less aggressive than the HCl medium, the protective coating is more noticeable and effective in this medium.

CONCLUSION

In this study, we have synthesized (E)-2-hydroxyethyl 3-(4-oxo-4H-chromen-3-yl) acrylate (HCAE) using dicyclohexylcarbodiimide (DCC) as the coupling agent. The compound was characterized using ^{1}H and ^{13}C-NMR spectroscopy. Examining the HCAE's resistance to corrosion at variable concentrations (100, 200, and 300 ppm) in 3.5% NaCl and 1M HCl media is the primary goal of electrochemical spectroscopy (EIS). Electrochemical spectroscopy (EIS) results at 303K showed that the HCAE inhibitor demonstrated remarkable inhibitory efficacy at 300 ppm, with 88.89% protection efficacy in 1M HCl and 93.88% protection efficacy in 3.5% NaCl. Additionally, the effectiveness of the HCAE in blocking corrosion was examined by analyzing the structural morphology of the protective layer that formed on the mild steel surface using scanning electron microscopy (SEM). The study highlights the HCAE's potential efficacy as a corrosion inhibitor in acidic and saline environments.

Author contributions

Meenakshi Sharma: Conceptualization, methodology design, data curation, formal analysis, and writing the original draft. Rakesh Kumar Tiwari: Supervision, Validation, writing editing. Sumit Kumar: Conceptualization, methodology design, supervision, validation, writing- review & editing.

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CONFLICT OF INTEREST STATEMENT

The author has no conflict of interest.

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