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Experimental Investigation of Inhibition on Mild Steel Corrosion in Two Different Acid Mediums by Synthesized Piperazin Derivatives

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ABSTRACT

Corrosion prevention studies show a predominant trend in the recent era. Especially mild steel material was used in many industrial sectors because it has specific properties like malleability and ductility. Corrosion inhibition action of a novel synthesized N-(1,3-benzothiazol-2-yl)-2-[4-furan-2-carbonyl)piperazin-2-yl]acetamide (1,3BFCPA) compound was performed on MS-mild steel material in 1 N HCl and 1 N H_2SO_4 medium. Using the mass loss data, the inhibitor efficiency has been evaluated on both the acidic and alkaline mediums. The inhibitor shows a maximum inhibitor efficiency on both acidic mediums, but when comparing 1N sulfuric acid, it shows a better efficiency of 90%. Based on surface coverage analysis (θ) from mass loss data, adsorption isotherms were interpreted to fit the behavior of the inhibitor over the surface of MS material, which shows a Langmuir adsorption isotherm.

Keywords: Mild steel, Corrosion inhibition, Novel inhibitor, Langmuir, Adsorption.

INTRODUCTION

To remove the scale deposited over the metal surface, it has been treated in acid pickling baths. The choice of inhibitors generally depends on the type of acid medium used, concentration, temperature, and nature of the metal chosen[1–3]. Organic-based inhibitors are known to be the best at protecting metals and equipment made of metal during transportation and storage[4–7]. Many researchers investigate corrosion inhibitor studies by using various synthesized organic compounds that contain heteroatoms, oxygen and sulphur atoms in their rings[8-11]. On a report of consumption productivity on copper and its combination, the benzotriazole compound shows a superior inhibition proficiency[12,13]. Three salts of Morpholine in particular Morpholine carbonate, phosphate, and borate, displayed 90% hindrance productivity, while outstanding salts showed an extremely low rate of 40% restraint proficiency[14,15]. In 1.11N Hydrochloric acid medium at three different temperatures, the synthesized Formazan derivative (FD) product was used as an inhibitor[16]. Using organic-based inhibitors that attribute an interaction with the surface of the metal via adsorption, either physical adsorption

or chemical adsorption, which forms a coordinate bond between metal and inhibitors[17], Therefore, in my investigation, (1,3BFCPA) was used as a corrosion inhibitor in 1N HCl and 1N H_2SO_4 medium at room temperature at estimated two-hour time intervals. Inhibitor studies were performed using weight loss methods, and results were confirmed by electrochemical studies. Adsorption studies also reveal a better result when using (1,3BFCPA) corrosion inhibitor on mild steel material.

MATERIALS AND METHODS

Chemistry
Synthesis of Primary Compound N-1, 3-benzo-thiazole-2-yl-2-chloro-acetamide

2-amino benzothiazole (1.5 g, 0.01 mole) and potassium carbonate (4.14, 0.030 mol) in 25 mL dimethylformamide chloroacetyl chloride (1.03 mL, 0.013 mol) was added slowly at Zero degree Celsius. The reaction was processed at room temperature (RT) for six hours with constant stirring. The reaction mixture was slowly added to ice water (150 mL) and extracted with acetooxyethane (2x150 mL). The combined layer of acetooxyethane was washed with water (1x200 mL) and saturated NaCl (1x200 mL). The concentrated acetooxyethane layer was carried out under reduced pressure. After the extraction, the solid product was thoroughly washed with diethyl ether to get the pure product N-1, 3-benzothiazol-2-yl-2-chloro-acetamide. Light brown solid; Yield 91%; m.p. 241-242°C.

Synthesis of N-(1,3-benzothiazol-2-yl)-2-[4-furan-2-carbonyl)piperazin-2-yl]acetamide

To the mixture of N-1, 3-benzo-thiazol-yl-2-chloro-acetamide (1 g, 0.0044 moles) and 1-(2-furoyl) piperazine (0.864, 0.0048 moles) in Dimethylformamide potassium carbonate (1.52 g, 0.011 moles) was added. For eight hours at 700 C, the resulting reaction mixture was heated. The hot reaction mixture was processed in a controlled manner using ice cooling and filtered. To the extracted filtrate, water (100 mL) was added and extracted with acetooxyethane (2x150 mL). The combined acetooxyethane was washed with brine solution (1x200 mL), desiccated on sodium sulfate and under reduced pressure it was concentrated. The resulting products were recrystallized from ethyl alcohol. Pale yellow solid; Yield 88%; m.p. 265-266°C. The synthetic route for the preparation of (1,3BFCPA)

is shown in Scheme 1. To get N-1, 3-benzothiazol-2-yl-2-chloro-acetamide, 2-aminobenzothiazole was reacted with 2-chloroacetyl chloride in the presence of Potassium carbonate.
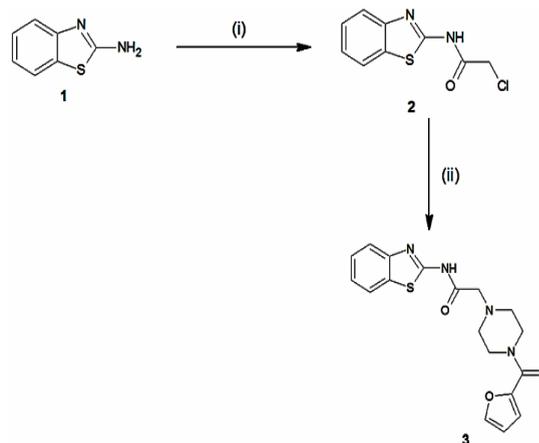
Scheme 1. Reagent and condition: (i). DMF, K_2CO_3, Chloroacetyl chloride, 0°C (ii). DMF, K_2CO_3, 1-(2-furoyl)piperazine, 70°C

Various concentration of inhibitor such as 10, 20, 40, 60, and 80,100ppm was prepared from the Stock solutions.

Specimen preparation (MS)

Mild steel material (MS) was cut into coupons of 5x1cm^2 having the percentage composition Iron-99.718, Nickel-0.012, Molybdenum-0.016, Chromium-0.038, Silicon-0.014, Phosphorus-0.011, Silicon-0.006, Manganese-0.171, Carbon-0.014.

Mass Loss Data

In 1N HCl and 1N H_2SO_4 at room temperature for two hours in various inhibitor concentrations, MS specimens were immersed. After the completion of two hours, the coupons were removed from the immersed medium, and washed with doubled distilled water and acetone. From the initial weight and final weight difference mass loss data was calculated. Mass loss data such as the rate of corrosion and the efficiency inhibitor was calculated using the formula,

Corrosion Rate (CR)=(87.6 x Difference in Weight)/(Density x Area x Time)

The efficiency of the Inhibitor (Inhibition efficiency),

Inhibition efficiency (IE)%=$[(W_o–W_i)/Wo]\times100$

Where (W_i) and (W_o) are the initial and final weight loss (in g) of MS in the inhibitor presence and absence respectively

Adsorption parameters

Langmuir adsorption isotherm was calculated using the parameters of adsorption such as ΔG_{ads}-free energy of adsorption, ΔH_{ads}-enthalpy of adsorption and ΔS_{ads}-adsorption entropy, which is presented in the following equation.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

Where C_{inh} is the concentration of the inhibitor used, K_{ads} is the Equilibrium Constant, and (θ)-Theta is surface coverage.

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C_{inh} - \frac{Q_{ads}}{2.303RT}$$

Where A is a constant, Q_{ads} is the adsorption of heat or enthalpy of adsorption.

K_{ads}-Equilibrium constant was calculated from the intercepts value of ($1/K_{ads}$) of the straight line received from the plot of Concentration of inhibitor/Surface coverage (θ) Vs Concentration of inhibitor. Adsorption of free energy was calculated using equilibrium constant value (K_{ads}) to the below

$$\Delta G_{ads} = -RT\ln(55.5K_{ads})$$

From the value, a direct line is obtained from the graph which is plotted between log ($\theta/1-\theta$) Vs 1000/T at many concentrations of inhibitor used. The slope is formed from the instant line which is $-\Delta H_{ads}/2.303R$. Enthalpy of activation (H_{ads}) calculated from the slop formed. The entropy of activation (ΔS_{ads}) is arrived from the equation.

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$

RESULT AND DISCUSSION

Mass Loss Data

After the preliminary process, MS specimens are polished with various ranges of emery sheets and punched with numbers at the top. Numbered plates were immersed in different concentrations of the inhibitor in 1N HCl and 1N H_2SO_4 medium for two hours at room temperature. From the weight loss data, the difference in weight of the plate before and after dipping it in the test solution was calculated and shown in Table 1.

Table 1: Corrosion parameter in the Presence and Absence of (1,3BFCPA) inhibitor on mild steel in different acidic medium solutions

| S. No | Conc. of inhibitor ppm | Acid medium | | | |
| | | 1N HCl | | 1N H₂SO₄ | |
		Rate of Corrosion (mmpy)	The efficiency of the inhibition (%)	Rate of Corrosion (mmpy)	The efficiency of the inhibition (%)
1	blank	19.8380	--	26.6366	--
2	10	7.1334	64.04	7.0231	73.63
3	20	6.4643	67.41	6.0183	77.40
4	40	5.4610	72.47	5.2380	80.33
5	60	4.1232	79.21	4.7922	82.00
6	80	2.8971	85.39	2.6743	89.96
7	100	2.5633	87.07	2.0061	92.46

Medium for two hours

The maximum inhibition efficiency of (1,3BFCPA was 87.07% in 1N HCl and 92.46% in 1N H_2SO_4 obtained at the optimum concentration (100ppm). With the addition of the inhibitor, a strong protective layer is formed on the surface of the metal. The rate of corrosion and efficiency of the inhibitor (1,3BFCPA) are represented in Figures 1 and 2.

Adsorption isotherm

The mass loss data calculated, which gives information about the interaction of the inhibitor (1,3BFCPA) on the surface of the metal coverage (θ) in 1N HCl and 1N H_2SO_4 for two hours at room temperature, is given in Table 2. A barrier is created for mass and rate change during the adsorption of (1,3BFCPA) on the MS surface. The situation prompted the protecting nature of a steel surface from the movement of serious particles in 1N HCl and 1N H_2SO_4 arrangement. The level of protection expanded with surface assurance by utilizing the adsorbed particles.
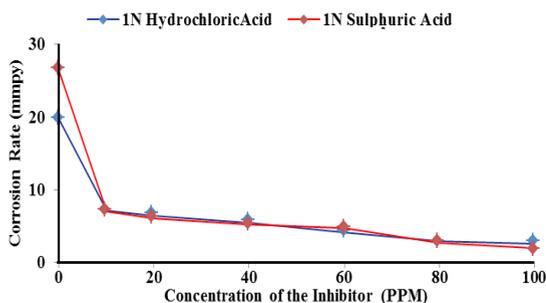
Fig. 1. Corrosion rate Comparison of (1,3BFCPA) inhibitor on mild steel in both acidic
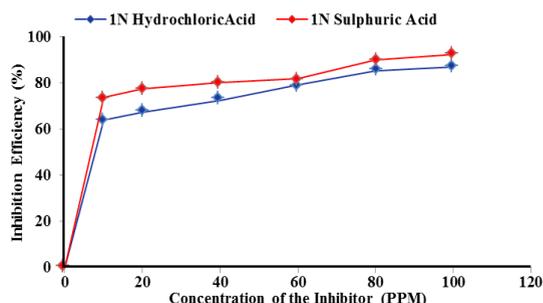
Fig. 2. Inhibition efficiency of (1,3BFCPA) inhibitor on mild steel in both acidic medium for two hours

Table 2: Adsorption isotherm parameters of (1,3BFCPA) on mild steel in both acidic medium

Inhibitor Concentration (M)	Acid medium	(1,3BFCPA) MS-Surface coverage(θ)	ΔG_{ads}(KJ/mol^{-1})	[Kx(10^{-2})]
Optimum concentration	1N HCl	0.87	-6.056	1.80
(100 PPM)	1N H$_2$SO$_4$	0.92	-5.031	1.79
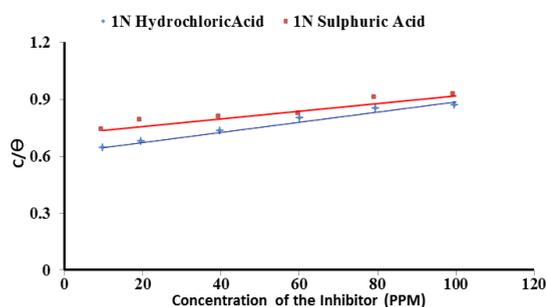
Fig. 3. Langmuir adsorption isotherm for adsorption of (1,3BFCPA) on mild steel in both acidic mediums

From Table 2 the data shows that there is no chemisorption, but there is physisorption between the inhibitor and metal surface in both acidic mediums. Fig. 3 clearly shows the fascination between the surface of the metal and inhibitor molecules. Adsorption of loose power (ΔG_{ads}), in 1N HCl and 1N H$_2$SO$_4$ became observed to be -6.056 kJmol^{-1} and -5.031 kJmol^{-1}. The values suggest physisorption takes place in the inhibitor structures.

CONCLUSION

Synthesized organic inhibitor synthesized N-(1,3-benzothiazol-2-yl)-2-[4-furan-2-carbonyl) piperazin-2-yl]acetamide (1,3BFCPA) shows better efficiency on both the acid medium 1N HCl and 1N H$_2$SO$_4$. On comparing the acidic medium efficiency of the inhibitor, it shows 92.46% on 1N H$_2$SO$_4$ compared to 1N HCl medium. Based on mass loss data the surface coverage (θ) is calculated Langmuir adsorption isotherm is obtained which shows a strong attraction between inhibitor and metal surface on both acidic mediums.

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Conflict of interest

The author declare that we have no conflict of interest.

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