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Synthesis, Characterization of 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide and its Synergistic Effect with Halide ions on the Corrosion Inhibition of Mild Steel in Acidic Medium

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Abstract

3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide has been synthesised and tested as corrosion inhibitor for mild steel in 2.5 M H_2SO_4. The synthesis of 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide was achieved by ethyl naphtho[2,1-b]furan-2-carboxylate. The title compound was characterised using FT-IR and ^{1}H NMR spectroscopy. The corrosion inhibition investigation has been conducted at 303K using Mylius thermometric technique. Results obtained showed that 3-nitronaphtho[2, 1-*b*]furan-2-carbohydrazide is the best inhibitor and its inhibition efficiency (E%) increases with the increase of inhibitor concentration and reaches up to 87% at 1% 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide. Inhibitor efficiency of 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide synergistically increases on addition of KCl, KBr and KI. The order of the inhibition is KI > KBr > KCl. The adsorption of 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide and its combination with halide ions on the metal surface was found to obey the Fruendlich, Temkin and Flory-Huggins adsorption isotherms at all temperatures studied. The values for the adsorption process show that the process is spontaneous.

Keywords: Corrosion, inhibition, mild steel, 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide, synergism, adsorption isotherm.

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Introduction

Mild steel is one of the most important widely used engineering materials due to its mechanical properties [1, 2] particularly for the structural and automobile applications. However, this metal is prone to corrosion attack [3-5] and its rate of corrosion is quite high in the presence of and aggressive medium such as acid, basic and salty solutions. Hence forth corrosion of mild steel is a fundamental academic and industrial concern that has received considerable amount of attention [6]. Some of the important fields of applications of acid solutions in industries being acid pickling of iron and steel, chemical cleaning, ore production and oil well acidification. Thus, the use of inhibitors is one of the most practical methods for protection against corrosion in acidic media [7]. Most of the well known acid inhibitors are organic compounds containing electron donor atoms particularly nitrogen, sulphur, oxygen in their functional groups with aromatic and heterocyclic rings. Organic compounds studied as inhibitors include benzatriazole [8], thiadiazolines [9], organic dyes [10,11] and some organic additives [12] to mention a few. These compounds act by adsorption of their molecules on the metal surface. Their action depends on the nature and surface change of the metal, nature of the medium and the chemical structure of the inhibitor.

The aim of this study was to investigate the corrosion inhibition of 3-nitronaphtho [2,1-*b*]furan-2-carbohydrazide. The 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide showed good performance as corrosion inhibitor in sulphuric acid medium due to the presence of heteroatom and unsaturated bond which cause effective adsorption process, leading to the formation of an insoluble protective surface film which suppresses the metal dissolution

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reaction. Furthermore, the molecule is big enough and likely to adsorb effectively on surface area (due to adsorption) and block the active sites and thereby reduce the corrosion rate [13].

3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide is used to synthesize β-lactam heterocycles which is one of the most prescribed antibiotics used in medicine. They are considered as an important contribution of science to humanity [14]. The 2-azetidinone (β-lactam) ring is an essential feature of a large number of biologically active compounds namely penicillins, cephalosporins, carumonam, aztreonam, thienamycine and the nocardicins [15]. Several methods have been reported to synthesize azetidinone derivatives of biological and pharmacological importance [16, 18]. Recently, the use of drugs as corrosion inhibitors for metals in various aggressive media has generated a lot of interest. Encouraged by this fact, it was contemplated to investigate for corrosion inhibition of mild steel using thermometric method. The synergistic effects of iodide additives on the corrosion inhibition of mild steel are also reported [10, 17]. Hence the effect of addition of halides on the inhibition efficiency of the inhibitor is studied.

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Experimental

Melting points were determined in open capillary tubes and are uncorrected. IR spectra(cm^{-1}) were recorded in KBr pellets on FT-IR Research Spectrophotometer Schimadzu 8201 PC(4000-400cm^{-1}) and NMR on Bruker DRX-300(300MHz-FT-NMR with low and high temperature facility -90^0 to $+80^0$).Standard chemical shifts are given in δ ppm values. Compounds were checked for their purity by TLC on silica gel plates and spots were visualized in iodine vapour

The synthesis of title compound was successfully accomplished through the following steps.

Step-1 Synthesis of ethyl 3-nitronaphtho[2,1-*b*]furan-2-carboxylate **2** using ethyl naphtho [2,1- *b*]furan-2-carboxylate **1**.

Step-2 Conversion of the nitro ester **2** into 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide **3.**

Synthesis of ethyl 3 -nitronaphtho[2,1-b]furan-2-carboxylate 2 :

A cooled nitrating mixture of con HNO_3 and con H_2SO_4 (1:2, 15 mL) was added very slowly to a cooled solution of ester **1** (2.4 g, 0.01 mol) in glacial acetic acid (4 mL) and the mixture was stirred for about 30 minutes at 0 to 15^oC. The stirring was continued for 2 h and the reaction mixture was poured on to crushed ice. The product, which separated as solid, was collected, dried and recrystallised from aqueous ethanol.

The IR spectrum exhibited characteristic absorption band at 1720 cm^{-1} due to ester carbonyl group and strong absorption band at 1535 cm^{-1} and 1354 cm^{-1} due to NO_2

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group. The structure of 2 was also established by recording ^{1}HNMR and comparing it with an authentic sample [18].

Synthesis of 3- nitronaphtho[2,1-b]furan-2-carbohydrazide 3 :

A mixture of ethyl 3-nitronaphtho[2,1-*b*]furan-2-carboxylate (2.55 g, 0.01 mol) and hydrazine hydrate (2.5 mL, 99%) in ethanol (10 mL) was heated under reflux for 5 h, cooled to room temperature and the solid thus separated was filtered, washed with ethanol and recrystallised from aqueous DMF to obtain the product as solid.

The structure of ethyl 3-nitronaphtho[2,1-b]furan-2-carbohydrazide **3** was established by its IR and ^{1}H NMR spectrum. The IR spectrum showed absorption band at 3335 $cm^{-1}$and 3278 cm^{1}due to amine/amide NH group, strong stretching band at 1650 cm^{-1} due to amide carbonyl and 1525cm^{-1} due to NO_2 group. ^{1}H NMR spectrum showed a singlet at δ 4.51 and δ 9.81 (D_2O exchangeable), which were accounted for NH_2 and NH protons. In addition it also exhibited a singlet at δ 2.01 and multiplet at δ 7.2 – 8.2 which were attributed to methyl and aromatic protons respectively.

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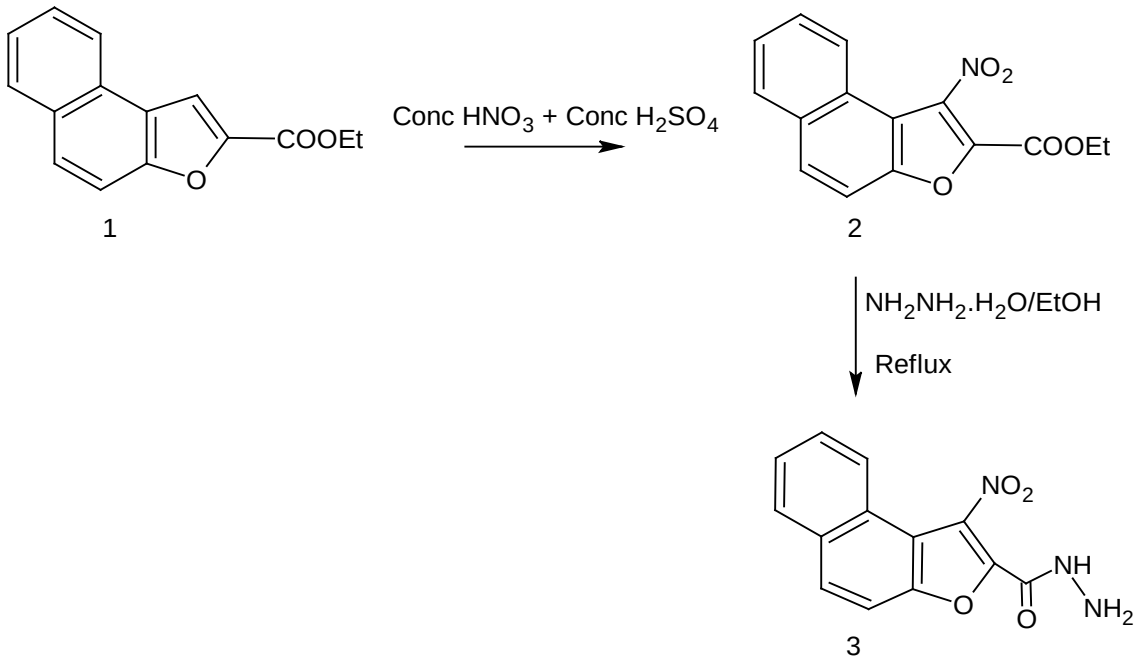

1 2 3

Mild steel metal (the percentage elemental composition was found to be, C(0.048%), Mn (0.335%), Si (0.029%), P(0.041%) ,S (0.025%), Cr (0.050%), Mo (0.016%), Ni (0.019%) and Fe (99.437%) having a surface area of 5x1cm^2 were cut from a large sheet. The specimens were polished successively with emery sheets, degreased and dried. Sulphuric acid were used for preparing solutions was AR grade. The specimens in triplicate were immersed in 1.5 M acid solutions containing various concentrations of the inhibitor for two hours at 300 K. The specimens were removed washed with water and dried. The mass of the specimens before and after immersion was determined using an electronic digital balance. The concentrations of the inhibitor (3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide) from 0.2 % to 1.0 % was prepared and used in the study. The concentrations of H_2SO_4 (blank) used were in the range 0.5 M – 2.5 M

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and Synergistic effects was studied in the presence of 0.05 M halide additives namely KCl, KBr, KI.

In this method, the mild steel specimen was completely immersed in blank and in combination with different concentrations of sulphuric acid, inhibitor and halides mixture. The volume of the test solution was kept at 100 mL. The initial temperature in all experiments was kept at 27^{o} C. The temperature was measured to ±0.05^{o} C on a calibrated thermometer (0-100^{o} C). This method allowed for the evaluation of the reaction number (RN). The RN is defined as

$$RN\ (Kmin^{-1}) = \frac{[T_m - T_i]}{t}$$

T_m =Maximum temperature attained by solution, T_i =Initial temperature of solution, t = time required to attain maximum temperature. The inhibition efficiency (IE %) was evaluated from percentage reduction in the reaction number using equation [19, 20]

$$IE\ \% = \frac{[RN_f - RN_i]}{RN_f} \times 100$$

Where, RN_f is the reaction number in free solution, RN_i is the reaction number in inhibited solution.

Results and Discussion

Effect of sulphuric acid concentration

In this part the weight loss-time curves of mild steel are constructed, under weight loss method. Fig.1 represents the variation of weight loss with time of mild steel immersed in H_2SO_4 of different concentrations range (0.5 to 2.5 M). Analysis of these curves shows that the weight loss (g/cm^3) increases with time along a period of 60 minute (immersion time), as well as upon increasing the concentration of all solutions under test.

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This may be attributed to the presence of water, air and H^+ which accelerate the corrosion process. This indicates that the corrosion rate of mild steel in test solutions is a function of the concentration of acid solution. This observation agrees with the fact that the rate of a chemical reaction increases with increasing concentrations.

The values of C.R, IE% and θ at different inhibitor concentrations are listed in Table 1. The data in table reveals that as the inhibitor concentration is increased, the corrosion rate decreases while the efficiency percent and surface coverage increases [21]. This behaviour may be attributed to be the increased surface coverage (θ) due to the increase in the number of adsorbed molecules on mild steel surface. A good efficiency is observed at constant concentration of inhibitor (1.0 %).

The effect of sulphuric acid concentration on the corrosion of mild steel is illustrated in the plot of temperature (^{o} C) against time (min) at different concentrations of H_2SO_4 as shown in Fig. 2. It is observed that the dissolution of mild steel begins after a time lag from the immersion of the coupons in the test solution. Also the temperature rises gradually with time and then decreases after reaching a maximum temperature (T_m). It is also observed that as the concentration of the sulphuric acid increases, temperature (T_m) increases and the time required to reach the maximum temperature decreases. This may due to the fact that increase in H_2SO_4 concentration gives rise to a corresponding increase in the concentrations of active species as well as increase in the rate of chemical reaction.

Temperature change of the system involving mild steel in 2.5 M H_2SO_4 is a function of time in the absence and presence of given concentrations of 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide (Fig. 3 and Table 2). The maximum temperature (Tm) measured in the free acid solution is 70 ^{o}C and was attained after time

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(t) of 20 min. This corresponds to a reaction number (RN) of 0.98 ^{o}C /min. Addition of 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide caused a decreased in the maximum temperature and an increase in the time required to reach it. This indicates that 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide retards the dissolution rate of mild steel in the acidic solution, may be due to adsorption on the metal surface. The extent of inhibition depends on the degree of coverage of the metal by the adsorbed molecules. Adsorption is noted for inhibitor, since a simultaneous increase in time and decrease in T_m takes place, and both the factors cause a large decrease in the reaction number RN of the system (Table 2) [22]. Increasing the inhibitor concentration in the acid solution decreases the RN of mild steel and consequently the inhibition efficiency is increased. This was confirmed by Freundlich's adsorption isotherm (Fig. 4)

The synergetic effects caused by halide ions are given in Table- 2.Figure-4 shows the temperature vs time curves for the dissolution of mild steel in different concentrations of 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide + halides mixture. A closer look at Fig. 5 shows a further reduction in the maximum temperature Tm, and a further increase in the time required to reach it. This shows that 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide in combination with iodide ions further retards the dissolution rate of aluminium in acidic medium when compared to 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide alone. The order of reactivity of halide ions is of the order KI > KBr > KCl. The inhibition efficiency increased 90 % to 95% at a concentration of 0.05 M KI and 1.0 % of inhibitor concentration. Thus this trend is confirmed by Freundlich's adsorption isotherm. (Fig. 6)

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Conclusion

3-Nitronaphtho[2,1-*b*]furan-2-carbohydrazide is found to be an inhibitor for mild steel corrosion in sulphuric acid medium. . Inhibition efficiency increased with increasing inhibitor concentration. The experimental data obtained in this study fits into Freundlich's adsorption isotherm. The addition of halides to 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide enhances the inhibition efficiency. The inhibition efficiency increased from 90.05 % to 95.51 % at a concentration of 0.05 M KI and 1.0 % of inhibitor concentration.

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Table 1. Effect of inhibitor concentration on corrosion rate (CR*)*, inhibition efficiency (IE %) and surface coverage (θ) of mild steel in 2.5 M H_2SO_4 at 27 ^{0}C .

Sl. No.	Concentration (%)	Weight loss(g)	Inhibition efficiency (%)	Degree of surface coverage (θ)	Corrosion rate (mpy)
1	Blank (2.5 MH_2SO_4)	0.069	-	-	6018.11
2	0.2	0.061	11.59	0.12	5320.36
3	0.4	0.032	53.62	0.54	2791.01
4	0.6	0.019	72.46	0.72	1657.16
5	0.8	0.012	82.61	0.83	1046.63
6	1.0	0.009	86.96	0.87	784.97

Table 2. Effect of 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide concentration on the parameters of the thermometric curves for mild steel in 2.5 M sulphuric acid.

Concentration of inhibitor	Ti (^{0}C)	Tm (^{0}C)	t (minutes)	Reaction Number , RN	Inhibition efficiency (%)
Blank (2.5 MH_2SO_4)	27.8	70.5	20	0.98	-
0.2 %	27.0	50.4	32	0.78	21.19
0.4 %	27.0	48.3	36	0.66	32.45
0.6 %	27.0	45.2	40	0.49	50.61

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0.8 %	27.1	41.5	44	0.46	52.78
1.0 %	27.0	37.2	48	0.22	77.37

Table 3. Synergistic effect of halides and 3-nitronaphtho[2,1-*b*]furan-2-carbohydrazide concentration on the parameters of the thermometric curves for mild steel in 2.5 M sulphuric acid.

System concentration	**Ti (^{0}C)**	**Tm (^{0}C)**	**t (minutes)**	**Reaction Number , RN**	**Inhibition efficiency (%)**
Blank (2.5 MH_2SO_4)	27.8	70.5	20	2.14	-
1.0 % inhibitor	27.0	37.2	48	0.90	90.05
1.0 % Inhibitor + 0.05 KCl	27.0	36.1	48	0.91	91.12
1.0 % Inhibitor + 0.05 M KBr	27.0	34.6	48	0.93	92.58
1.0 % Inhibitor + 0.05 % KI	27.1	31.6	48	0.96	95.51

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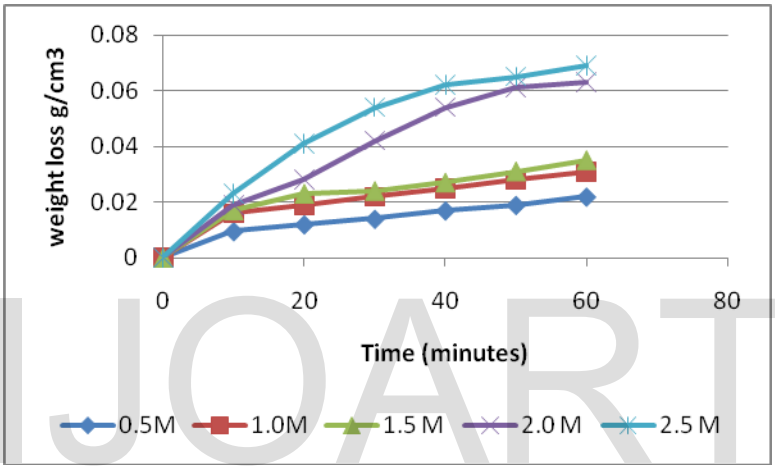

Figure 1

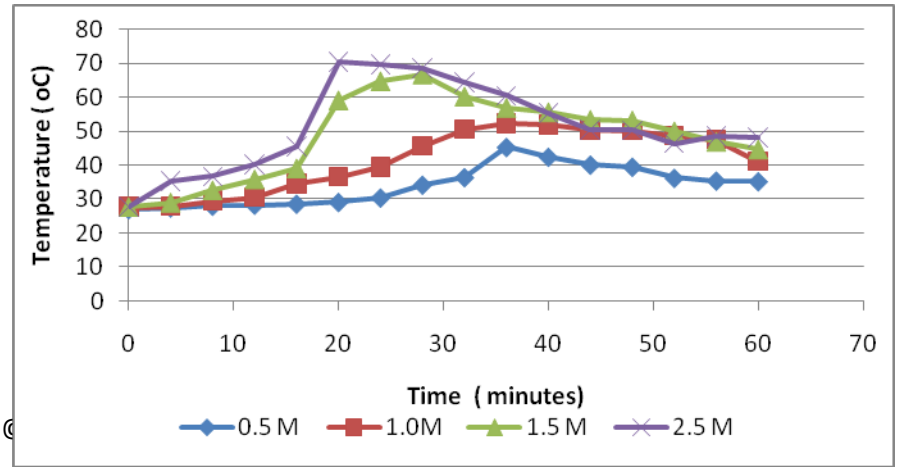

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Figure 2

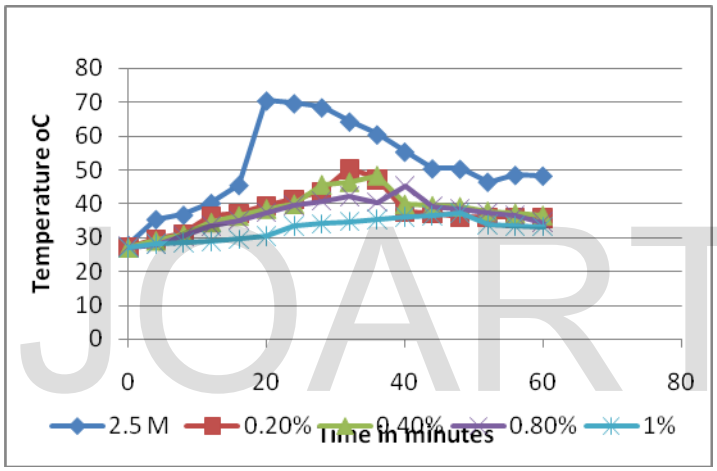

Figure 3

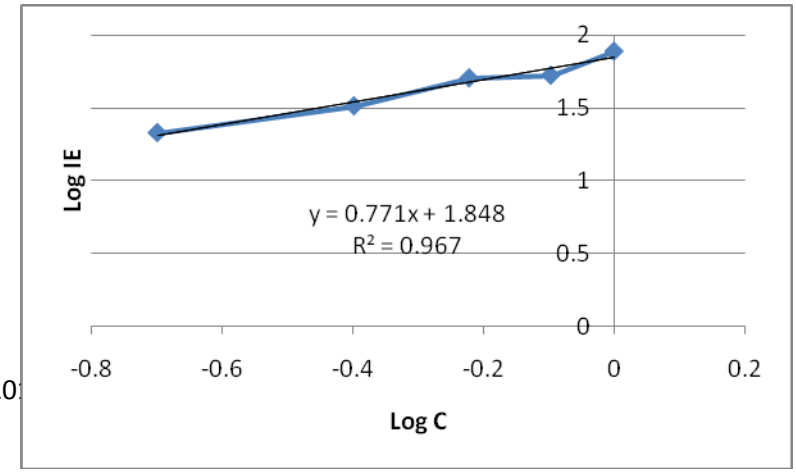

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Figure 4

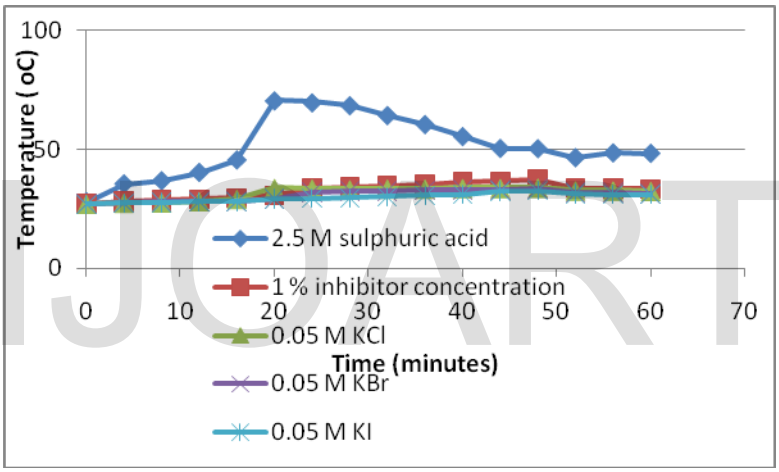

Figure 5

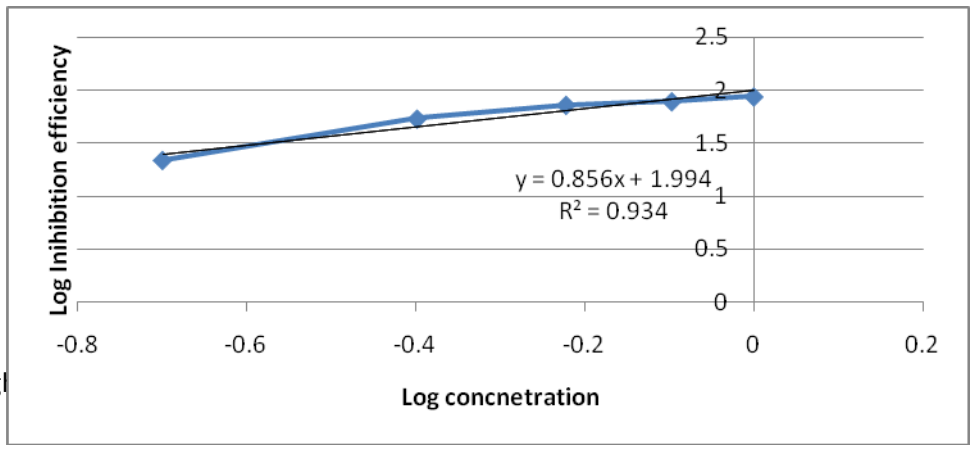

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Figure 6

Legends to Figure

Figure 1. Weight loss-time curves for mild steel in solutions of different concentrations of sulphuric acid.

Figure 2. Variation of temperature with time for the dissolution of mild steel in given concentrations of H_2SO_4 (Blank).

Figure 3. Effect of 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide concentration on thermometric curves of mild steel in 2.5 M sulphuric acid.

Figure 4. Log IE vs log C in the presence of inhibitor.

Figure 5. Synergistic effect of 0.05 M halides in presence of 2.5 M sulphuric acid and of 1.0 % of 3-nitronaphtho[2,1-*b*]furan-2- carbohydrazide.

Figure 6. Log IE vs log C in the presence of inhibitor and potassium Iodide.

