

## Research Article

# Inhibition of Corrosion of Aluminium in Potassium Hydroxide Solution by Pyridine Derivatives

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The influence of 3-methylpyridine and 3-nitropyridine on the corrosion rate of aluminium in 1 mol L<sup>-1</sup> potassium hydroxide solution was investigated using weight loss method. It was observed that both investigated derivatives behave as inhibitors. It was found that the inhibition efficiency increases with increasing inhibitor concentration. The inhibition mechanism is discussed on the basis of adsorption of inhibitor molecules on the metal surface. The inhibitors were adsorbed on the surface according to the Frumkin adsorption isotherm. The effect of temperature on the corrosion inhibition of Al was studied and thermodynamic functions for the dissolution and adsorption processes in the absence and in the presence of the inhibitors were computed and discussed.

## 1. Introduction

Aluminium is widely used in industry because of its low density, pleasing appearance, and corrosion resistance nature. During industrial process it often comes in contact with corroding solutions. Therefore, corrosion creates serious troubles in the industry [1]. For these reasons, various workers have explained the corrosion inhibition of aluminium in different solutions [2–10]. A useful method to protect metals deployed in service in corrosive environment is the adsorption of species on the surface of metal in order to inhibit the corrosion reaction and reduce the corrosion rate. The extent of adsorption depends on the nature of the metal, the condition of the metal surface, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosive media [11].

Among the various methods used in treating corrosion problems, the use of chemical inhibitors is the most cost effective and practical method. The use of corrosion inhibitors based on organic compounds containing nitrogen, sulfur, and oxygen atoms is of growing interest in the field of corrosion and industries, as corrosion causes serious problems to the service lifetime of alloys used in industry [12]. The stability of

the adsorbed inhibitor films formed on the metal surface to protect the metal from corrosion depends on physicochemical properties of the molecule, such as aromaticity, steric effects, electron density of donor atoms, as well as the type of corrosive medium, and the nature of the interaction between the inhibitor and the metal surface [13–15].

A number of organic compounds are known to be applicable as corrosion inhibitors in alkaline environment. However there is no report on influence of pyridine derivatives as corrosion inhibitors. As a part of our contribution to the growing interest of exploring inhibition of aluminium, the present study investigates the inhibitive effect of 3-methylpyridine and 3-nitropyridine on aluminium in 1 mol L<sup>-1</sup> KOH, using weight loss method in the temperature range of 20–50°C.

## 2. Materials and Method

**2.1. Materials Preparation.** The sheet of aluminium used for this study has the following chemical composition (wt.%): Al (99.95%), Cu (0.01%), Mg (0.02%), Si (0.02%), Mn (0.002%), and Zn (0.005%), and it was obtained commercially from Jindal Aluminium Limited, India. The inhibitors used

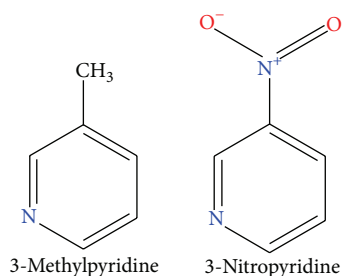


FIGURE 1: Chemical structure of inhibitor compounds.

TABLE 1: Elemental analysis.

Derivative	Yield %	Elemental analysis		% N
		% C	% H	
3-Nitropyridine	81.0	48.42 (48.39)	3.15 (3.25)	22.20 (22.57)

\*Theoretical percentage of element is stated in the bracket.

were 3-nitropyridine and 3-methylpyridine derivatives with chemical structure shown in Figure 1.

**2.1.1. Preparation of Inhibitor Used.** 3-Methylpyridine (derivative 2) was obtained from Research Lab fine chem. Industries, Mumbai, and used as it is. Another derivative, 3-nitropyridine, (derivative 1) was synthesized in the laboratory.

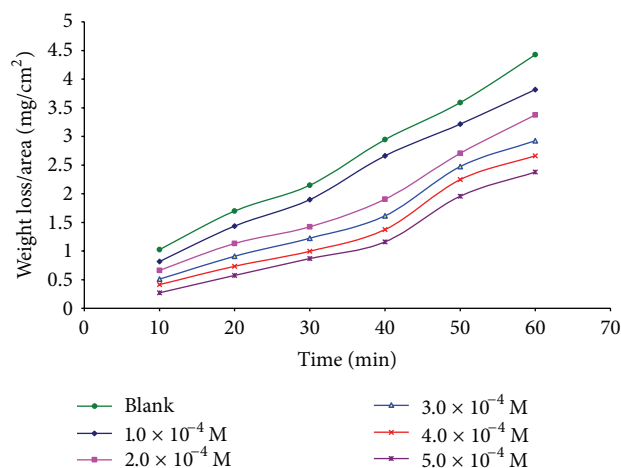
**Synthesis of 3-Nitropyridine (Derivative 1).** For the preparation of 3-nitropyridine, various chemicals of A.R. grade are used.  $10.0 \text{ cm}^3$  of  $0.042 \text{ mol L}^{-1}$  trifluoroacetic anhydride was chilled in the ice-bath and  $0.017 \text{ M}$  pyridine was slowly added to it. The mixture was stirred at chilled conditions for 2 hours. Then  $2.0 \text{ cm}^3$  of  $0.036 \text{ mol L}^{-1}$  concentrated nitric acid was added dropwise. The mixture was stirred for 9 hours; then it was dripped slowly into a chilled aqueous solution of  $0.017 \text{ mol L}^{-1}$  sodium metabisulfite. After 24 hours, the solution was extracted with methylene chloride and the extract was dried over anhydrous sodium sulphate. After evaporation of the solvent, 3-nitropyridine was obtained. Formation of 3-nitropyridine was established by elemental analysis in Table 1.

The purity of 3-nitropyridine was tested by melting point. This derivative was further used as inhibitor of corrosion of aluminium in  $1 \text{ mol L}^{-1}$  KOH.

The stock solution of  $10^2 \text{ mol L}^{-1}$  of 3-methylpyridine and 3-nitropyridine was prepared by dissolving an accurately weighed quantity of each in double distilled water. From this stock solution, required concentrations ranging from  $1.0 \times 10^{-4}$  to  $5.0 \times 10^{-4} \text{ mol L}^{-1}$  were prepared by dilution.

## 2.2. Chemical Technique

**2.2.1. Weight Loss Method.** The weight loss measurements were carried out as described elsewhere [16, 17]. Weight loss measurements were conducted under total immersion condition in  $200 \text{ cm}^3$  of test solutions ( $1 \text{ mol L}^{-1}$  KOH)

FIGURE 2: The weight loss versus time for Al corrosion in  $1 \text{ mol L}^{-1}$  KOH in the presence of different concentrations of 3-nitropyridine.

maintained at  $20\text{--}50^\circ\text{C}$ . Six metal pieces were cut into  $5 \text{ cm} \times 5 \text{ cm} \times 0.5 \text{ cm}$  in dimension and labelled as A, B, C, D, E and F. They were first polished with a coarse paper and then with emery paper, degreased in alcohol, rinsed in double distilled water, and finally dried in oven and weighed.

Each coupon was dipped separately in a beaker containing  $200.0 \text{ cm}^3$   $1 \text{ mol L}^{-1}$  potassium hydroxide solutions, and simultaneously stopwatch was started. The initial time of dipping was recorded. Coupon "A" was removed after 10 minutes and washed with tap water and then with distilled water. It was dried in air and again washed with acetone. Finally, it was dried in hot air. Subsequently, the coupons B, C, D, E, and F were also removed at time intervals of 20, 30, 40, 50, and 60 minutes, respectively. Thus, all six coupons were removed at regular time intervals and washed with tap water and distilled water. They were dried in air, again washed with acetone, and finally dried in hot air. All the coupons were weighed on an analytical balance to an accuracy of 5% and their final weight was recorded.

In another experiment, a set of fresh coupons was immersed in the flask containing  $1 \text{ mol L}^{-1}$  KOH and different concentrations of inhibitor derivative (1 or 2). The study was conducted at  $20$  and  $50^\circ\text{C}$  maintained using a thermostated water bath. Each experiment was repeated three times to ensure reproducibility, and the average values are reported.

## 3. Results and Discussion

Figures 2 and 3 show the weight loss time plots for Al in  $1 \text{ mol L}^{-1}$  KOH solution in presence and absence of various concentrations of the two derivatives (1 and 2) at  $20^\circ\text{C}$ . The plots are characterized by the increase in weight loss plots for added derivatives (1 and 2) containing system fall below that of the blank. The result shows that, by increasing the concentrations of 3-nitropyridine and 3-methylpyridine, the inhibition of corrosion of aluminium increases. The inhibition efficiency was calculated at each concentration.

TABLE 2: Inhibition efficiency of 3-nitropyridine.

Sr. number	Time (min)	Inhibition efficiency (%) of 3-nitropyridine				
		$1.0 \times 10^{-4} \text{ mol L}^{-1}$	$2.0 \times 10^{-4} \text{ mol L}^{-1}$	$3.0 \times 10^{-4} \text{ mol L}^{-1}$	$4.0 \times 10^{-4} \text{ mol L}^{-1}$	$5.0 \times 10^{-4} \text{ mol L}^{-1}$
1	10	20.31	35.55	50.29	59.67	73.63
2	20	15.50	33.29	46.38	56.75	66.18
3	30	11.68	33.83	43.14	53.75	59.56
4	40	9.61	35.30	45.21	53.39	60.59
5	50	10.42	24.63	31.04	37.36	45.50
6	60	13.80	23.76	33.95	39.89	46.31

TABLE 3: Inhibition efficiency of 3-methylpyridine.

Sr. number	Time (min)	Inhibition efficiency (%) of 3-methylpyridine				
		$1.0 \times 10^{-4} \text{ mol L}^{-1}$	$2.0 \times 10^{-4} \text{ mol L}^{-1}$	$3.0 \times 10^{-4} \text{ mol L}^{-1}$	$4.0 \times 10^{-4} \text{ mol L}^{-1}$	$5.0 \times 10^{-4} \text{ mol L}^{-1}$
1	10	30.27	45.51	60.25	69.63	83.59
2	20	21.51	39.30	52.39	62.76	72.19
3	30	16.43	38.58	47.88	58.49	64.31
4	40	13.07	38.76	48.68	56.86	64.05
5	50	13.26	27.47	33.88	40.21	48.34
6	60	13.80	28.35	38.99	46.31	53.35

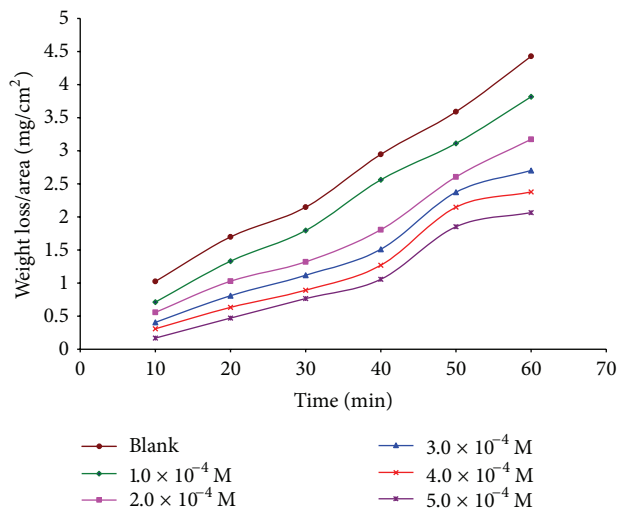


FIGURE 3: The weight loss versus time for Al corrosion in  $1 \text{ mol L}^{-1}$  KOH in the presence of different concentrations of 3-methylpyridine.

The inhibition efficiency was given by the following: inhibition efficiency =  $100(1 - W_i/W_f)$ , where  $W_i$  = weight loss in presence of derivatives and  $W_f$  = weight loss in absence of derivatives. It was observed that, by increasing the concentration of 3-nitropyridine and 3-methylpyridine, there is significant increase in the inhibition efficiency.

Tables 2 and 3 show that inhibition efficiency of added derivatives (1 and 2) increases with the increase of their concentration in  $1 \text{ mol L}^{-1}$  KOH solution. Hence, it is quite obvious that the increase in surface area coverage by added derivatives (1 and 2) decreases the dissolution of aluminium

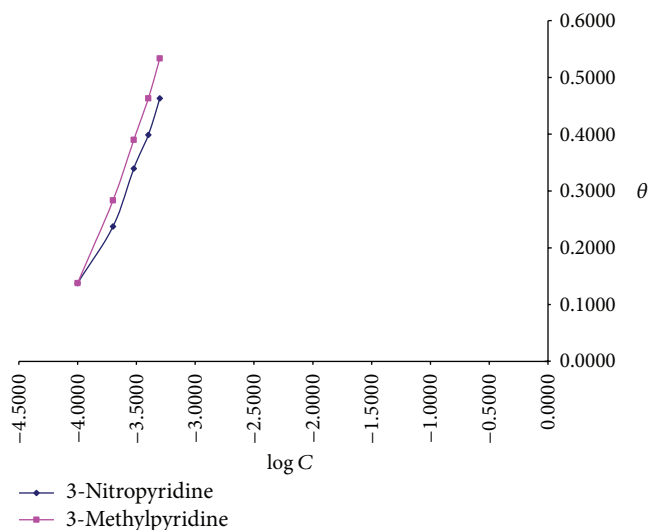
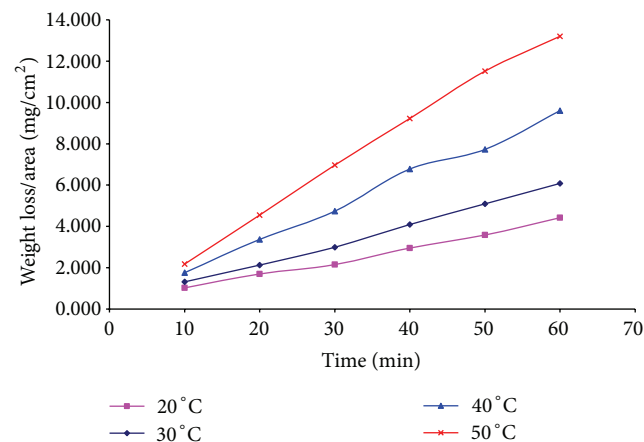
in  $1 \text{ mol L}^{-1}$  KOH solution. Also the rate of a chemical reaction decreases with time; therefore, as the time duration increases, the inhibition efficiency also decreases. It is observed that the inhibition efficiency of 3-methylpyridine in  $1 \text{ mol L}^{-1}$  KOH solution, over all the concentration ranges, is greater than that of the 3-nitropyridine.

**3.1. Adsorption Considerations.** The inhibition of Al corrosion in the presence of the added pyridine derivatives (1 and 2) has been attributed to their adsorption onto the Al surface which depends upon the charge, the nature and the electronic characteristics of the metal surface, adsorption of solvent molecules and other ionic species, temperature, and the electrochemical potential at the solution interface [18]. The adsorption of inhibitors is confirmed from the fit of the experimental data to various adsorption isotherms. It was found that the best fit was with Frumkin's isotherm which is  $\theta = k + (2.303/f) \log C$ , where  $k$  is the constant and  $f$  is free energy of adsorption. When plot of  $\theta$  versus  $\log C$  was plotted for the added derivatives (1 and 2), Frumkin's isotherm is obeyed as shown in Table 4 and Figure 4.

**3.2. Effect of Temperature.** The dissolution of Al in  $1 \text{ mol L}^{-1}$  KOH solution increases by increasing temperature from 20 to  $50^\circ\text{C}$  (Figure 5). The dissolution study was carried out in the presence of pyridine derivatives (1 and 2) at  $1.0 \times 10^{-4} \text{ mol L}^{-1}$  by weight loss method over a temperature range of  $20\text{--}50^\circ\text{C}$ . The weight loss time obtained in the presence of derivatives (1 and 2) shows that the rate of Al dissolution increases as temperature increases, but at lower rate than depicted in Figure 5. It is observed that the inhibition efficiency of added derivatives (1 and 2) decreases with increasing temperature which shows that the adsorption

TABLE 4: Adsorption study of inhibitors.

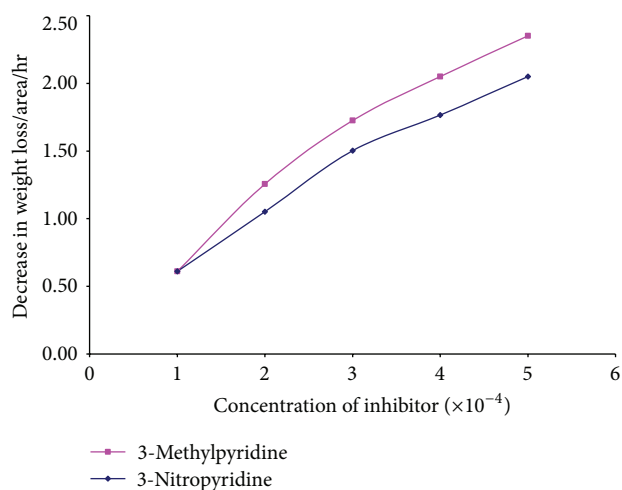
Sr. number	Concentration of inhibitor (mol L <sup>-1</sup> )	log C	$\theta$	
			3-Nitropyridine	3-Methylpyridine
1	$1.0 \times 10^{-4}$	-4.0000	0.1380	0.1380
2	$2.0 \times 10^{-4}$	-3.6989	0.2376	0.2835
3	$3.0 \times 10^{-4}$	-3.5228	0.3395	0.3899
4	$4.0 \times 10^{-4}$	-3.3979	0.3989	0.4631
5	$5.0 \times 10^{-4}$	-3.3010	0.4631	0.5335

FIGURE 4: Adsorption study of the corrosion of Al in 1 mol L<sup>-1</sup> KOH in presence of inhibitors.FIGURE 5: The weight loss versus time for Al corrosion in 1 mol L<sup>-1</sup> KOH in the absence of inhibitor at different temperatures.

of both derivatives on the surface of Al occurs through physical adsorption. Desorption takes place by increasing the system temperature. The value of activation energy,  $E_a^*$ , for the blank 1 mol L<sup>-1</sup> KOH solution was calculated and found to be 28.24 KJ mole<sup>-1</sup>. The activation energy in presence of derivatives (1 and 2) was also calculated and it is found to be

TABLE 5: Inhibition coefficient.

Sr. number	Concentration of inhibitor (mol L <sup>-1</sup> )	Decrease in wt. loss/area/hr with respect to blank (mg/cm <sup>2</sup> )	
		3-Nitropyridine	3-Methylpyridine
1	$1.0 \times 10^{-4}$	0.611	0.611
2	$2.0 \times 10^{-4}$	1.052	1.257
3	$3.0 \times 10^{-4}$	1.503	1.726
4	$4.0 \times 10^{-4}$	1.766	2.050
5	$5.0 \times 10^{-4}$	2.050	2.352

FIGURE 6: Decrease in weight loss with respect to blank versus concentration of inhibitors for corrosion of Al in 1 mol L<sup>-1</sup> KOH solution (inhibition coefficient).

36.22 KJ mole<sup>-1</sup> and 39.34 KJ mole<sup>-1</sup>, respectively. The result shows higher values of energy of activation  $E_a^*$  in presence of inhibitors. This is because the adsorption of inhibitors takes place at the higher energy sites, blocks the active sites, and increases the activation energy [19]. It also shows that increase in inhibition efficiency increases the energy of activation. It suggests exothermic nature of the dissolution process and dissolution of Al in 1 mol L<sup>-1</sup> KOH solution becomes difficult.

**3.3. Inhibition Coefficient.** Decrease in weight loss (blank minus inhibitor) in presence of the two derivatives at various concentrations occurs as given in Table 5. These decreases in weight loss were plotted versus concentration of both derivatives. Straight lines were obtained as shown in Figure 6.

The slope of these lines could be considered as “inhibition coefficient.” It is observed that the “inhibition coefficient” for 3-nitropyridine is less than 3-methylpyridine.

#### 4. Conclusion

Pyridine derivative compounds inhibit the corrosion of Al in  $1 \text{ mol L}^{-1}$  KOH solutions. The inhibition efficiency of these compounds increased with increasing concentration of the inhibitor and decreasing temperature. The inhibition action of these compounds is attributed to adsorption of inhibitor molecules on the metal surface. The adsorption process was found to obey the Frumkin adsorption isotherm. The inhibition efficiency of 3-methylpyridine is greater than that of 3-nitropyridine.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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