Inhibition of corrosion of mild steel in sulphuric acid by 2-Picoline N-Oxide and 4-Picoline N-Oxide

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Abstract: The present study aims at the synthesis of 2-Picoline N-Oxide (2-PiNO) and 4-Picoline N-Oxide (4-PiNO) and the study of their inhibition behaviour on the corrosion of mild steel in sulphuric acid. The selected compounds were synthesised and tested by subjecting to the weight loss studies, polarisation studies and Electrochemical Impedance Spectra (EIS) for assessment of their performance as corrosion inhibitors. The studies were made with 2N sulphuric acid with the inhibitor concentration in the range of 50-350 ppm. The adsorption of 2-Picoline N-oxide and 4-Picoline N-oxide on the mild steel surface obeyed the Longmire adsorption isotherm. Potentiodynamic polarization curves showed that of 2-Picoline N-Oxide and 4-Picoline N-Oxide acted as a anodic inhibition predominantly in sulphuric acid. This was supported by the impedance measurements which showed a change in the charge transfer resistance and double layer capacitance indicating adsorption of 2-Picoline N-Oxide and 4-Picoline N-Oxide on the mild steel surface. Scanning electron microscopy (SEM) technique is used to confirm the effectiveness of inhibition of mild steel in sulphuric acid medium. The results indicate that the synthesised inhibitors performed better in the chosen corroding medium and function by adsorption or by the formation of a protective film over the metal surface.
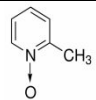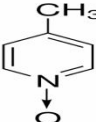**Keywords:** Mild steel, Corrosion inhibition, 2-PiNO, 4-PiNO.

Introduction

Corrosion problems have received a considerable amount of attention because of their attack on materials. The use of inhibitors is one of the most practical methods for protection against corrosion (1). Corrosion inhibition of mild steel by ethyltriphenylphosphoniumiodide in acid medium was studied by Goswami(2). Acid solutions are widely used in industry. Some of the important fields of application being acid pickling of iron and steel, chemical cleaning and processing, ore production and oil well acidification. In acidic media, the use of hydrochloric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble-free compared to other mineral acids(3). Mild steel is used extensively in industries but prone to corrosion in the applications involving the handling of sulphuric acid. Many synthetic and green inhibitors (4-14) have been tried with the corrosion of mild steel in sulphuric acid medium. Each inhibitor has its own merits and demerits. Picolines have been tried as Inhibitors of corrosion (15). The quantum chemical test mild steel of their behaviour has been discussed. Synthetic inhibitors pose the problem of high cost because of the costlier raw materials involved and also the toxicity exhibited by them. Natural plant extracts have been tried as green inhibitors so that they are reasonably non- toxic and easy to extract compared to the synthetic methods. Corrosion inhibitors are either synthesised or extracted from the plants by refluxing

with water or alcohol or a suitable solvent miscible with water. The extract concentrate is too difficult to be assessed in terms of concentration of concentration for natural plant extracts.

The present study focuses on the synthesis of 2-Picoline N-oxide (2-PiNO) and 4-Picoline N-Oxide (4-PiNO) and testing the synthesised compounds for their corrosion inhibition behaviour. Synthesised compounds are tested by FTIR spectra for their characterization. The compounds were then dissolved in minimum amount of alcohol and then suitably diluted to get the desired concentration. Mild steel specimens of specific areas were then immersed in these inhibitors in sulphuric acid medium and tested with weight loss studies, polarisation studies and Electrochemical Impedance Spectra (EIS) techniques.

Name of the inhibitor	Molecular formula	Structural formula	Molecular weight
2-Picoline N-Oxide(2-PiNO)	C_6H_7NO		109
4-Picoline N-Oxide(4-PiNO)	C_6H_7NO		109

Experimental

1. Synthesis of inhibitors

2-Picoline N-Oxide and 4-Picoline N-Oxide were synthesised using the method reported in the literature (16). To a mixture of 2-Picoline (200 mg), molecular sieve catalyst (10 mg) and solvent water (10 ml) at a temperature of 60° C, 30% dilute hydrogen peroxide (1:2 or 1:4 molar ratio) was added drop wise. The course of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the catalyst was separated by filtration. The excess solvent was removed by distillation at high vacuum and the product was separated by column chromatography using silica gel column packed with 15% methanol in chloroform. The same procedure was repeated with 4-Picoline N-Oxide acid as the raw material to get the compound 4-Picoline N-Oxide (4-PiNO). The compounds 2-PiNO and 4-PiNO were analyzed by FTIR spectroscopy using the instrument, NICOLET IS5 model, Thermo scientific instrument, USA.

2. Weight loss studies

a) Preparation of specimens

Mild steel specimens were cut into rectangular strips with typical dimensions of 1 cm^2 area. The chemical composition of mild steel used was Cu-0.14%, Mn-0.35%,Si-0.17%, S-0.025, P-0.03%, and the remainder iron (17). These specimens were then abraded with different grade emery papers washed with acetone and distilled water, dried and weighed to get constant weight.

b) Weight Loss Measurement

The weighed mild steel specimens were suspended by means of glass hooks in a beakers containing 2N sulphuric acid with various concentration of inhibitors. After the specified periods of immersion (1, 2, 6 and 24 hours) the specimens were taken out, washed in running water, dried and weighed. The inhibition efficiency and the corrosion rate were calculated from the observed weight losses using the following relationships (18, 19).

Corrosion Inhibition efficiency (IE) was then calculated using the equation.
$$\% \ IE=100[1-W_2/W_1] \ \%$$
Where W_1=weight loss in the absence of the inhibitor and W_2= weight loss in the presence of the inhibitor.

$$\text{Corrosion rate} = \frac{\text{Loss in weight(mg)}}{\text{Surface area of the specimen (dm}^2) \ x \ \text{Period of immersion(days)}}$$

3. Polarization studies

Polarization studies for the mild steel specimens were carried out with a CHI electrochemical workstation, Model 650C, USA. A three electrode cell assembly was used. The working electrode was mild steel specimen of 1cm^2 area. Saturated calomel electrode (SCE) was used as the reference electrode and platinum strip was used as the counter electrode for the polarization study. The corrosion parameters of the working electrode (mild steel) such as corrosion potential (E_{corr}), corrosion current (I_{corr}) and Tafel slopes (ba and bc) were calculated, for the cases of mild steel working electrodes in sulphuric acid electrolytes with optimal concentrations of the inhibitors.

4. AC impedance measurements

CHI electrochemical workstation, Model 650C, USA, was used to record AC impedance measurements. A three electrode cell assembly was used. The working electrode was a rectangular specimen of mild steel with one face of the electrode of constant 1cm^2 area exposed. A rectangular foil of platinum was used as the counter electrode. The three electrode assembly was placed in a glass cell provided with provisions for enclosing the electrolyte. The corrodent (2N H_2SO_4) was filled in the glass cell with or without inhibitors (at their optimal concentration). A time interval of 5 to 10 min was given for the system to acquire the open circuit potential. Then a steady state potential of 10mv was superimposed as the electrode under test. The AC frequency was varied from 0.1 to 10^5 Hz same retention was allowed for the electrode to attain its equilibrium potential (open circuit potential) .The potentials were then scanned at a particular sweep as either direction anodic and cathodic to its equilibrium potential. The results were plotted as strip-chart recorder of polarization unit, and of the cell impedance were measure in ohm for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. The double layer capacitance ($C_{dl)}$ was calculated using the following relationship.

$$C_{dl} = \frac{1}{2 \times 3.14 \times f_{max}}$$

5. Scanning Electron Microscopy

The study of Scanning Electron Microscopy of the mild steel specimen in the absence and in the presence of these inhibitor species were carried out using a Digital Scanning Electron Microscope model Hitachi, Japan Model No: SN 3000. Make with an accelerating voltage of 5 KV between the scan speeds and micrographs were taken at the magnitudes ranging from 350 X to 2000 X.
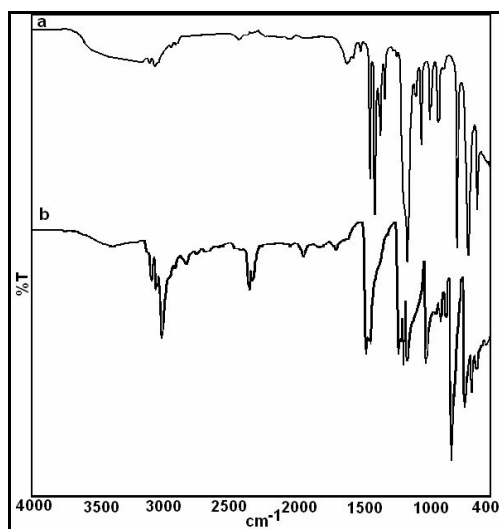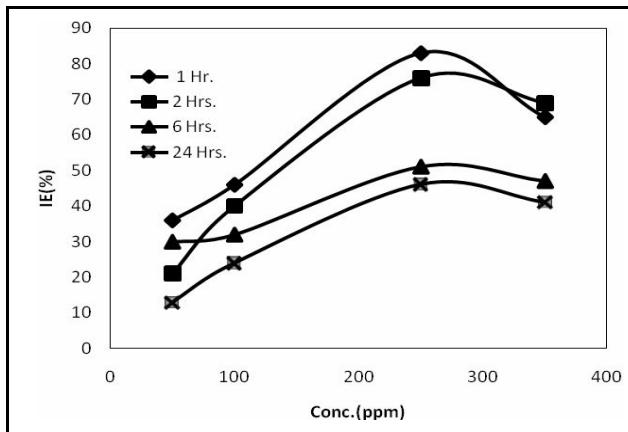
Results and discussion

1. FTIR Spectra

Fig 1. FTIR Spectra of (a) 2-PiNO and (b) 4-PiNO

Fig.2. Inhibitor Efficiency of 2- PiNO

The FTIR Spectra of the synthesised inhibitors 2PiNO and 4PiNO are shown in fig. 1 & 2. The presence of characteristic IR absorption at 3086 cm^{-1} and 2895 cm^{-1} respectively aromatic C-H and aliphatic C-H confirm the heterocyclic six membered ring with hetero atom and the carboxylic acid substituent at the meta and para (3,4) position (≈1200 cm^{-1}) with respect to the hetero atom nitrogen. It is evident that the N→O group and the aromatic ring exhibit characteristic peaks at 1236 cm^{-1} and 3000 cm^{-1} respectively. It is to be noted that the N → O Coordination is more ionised in the 2-PiNO isomer compared to the 4-PiNO isomer. The increased degree of dissociation for the 2-PiNO isomer is attributed to the electro-releasing alkyl (methyl) group in the ortho-position to the hetero-atom (nitrogen).

**2. Weight loss measurements**
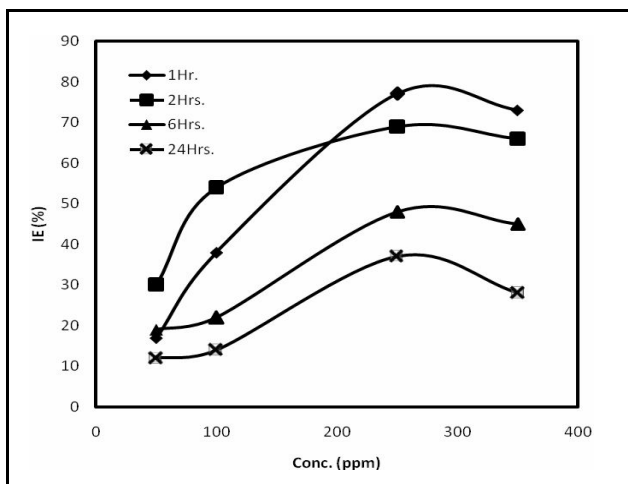
Fig.3. Efficiency of inhibitor - 4 PiNO

The inhibition efficiencies of the inhibitors under various concentrations studied, at different times of immersion in the corroding medium 2N H_2SO_4. The figure 2&3 shows the variation of the weight loss of the specimen at different times of immersion in the corroding medium (blank-without inhibitors). It is evident from the figures that the both inhibitors perform reasonably better. Among the two inhibitors 2-PiNO performs better than 4-PiNO as the corrosion inhibitor for mild steel in 2N H_2SO_4. During the concentration variation the inhibitor efficiency increased upto 250 ppm then slowly decreased it is may be act as reversible action on mild steel.

The better performance of 2-PiNO, compared to 4-PiNO as corrosion inhibitor, may be attributed to the better adsorptive forces established due to the electrostatic interaction between Fe^{2+} ions formed initially due to the slight onset of corrosion of mild steel and lone electron pair of oxygen of nitrones (N→O:) of the 2-PiNO compound, compared to the coordinated oxygen of the 4-PiNO isomer.

3. Polarization studies

The polarization studies for mild steel specimens in blank and the optimum concentrations of the inhibitors. It is evident from the figure 4 that the corrosion potential is influenced much but the corrosion current is reduced in the presence of inhibitors. It indicates that the rate of corrosion is reduced in the presence of inhibitors, proportional to their concentrations.
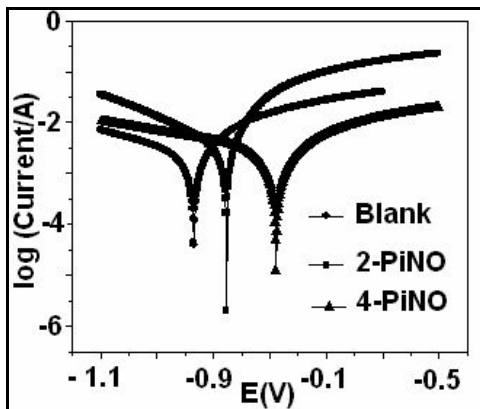
Fig 4. Polarization curves of mild steel immersed in 2N H_2SO_4 + Inhibitors a) 2-PiNO b) 4 -PiNO

Thus the inhibitors function by adsorption on to the metal surface. The extent of adsorption is improved due to electrostatic forces established between the Fe^{2+} ions formed on the mild steel surface, due to the initial, slight but unavoidable corrosion of the mild steel (Ferrous alloy), whereas the adsorptive forces are stabilised between the lone pair of electrons of oxygen atom of 2-PiNO isomer and Fe^{2+} of the mild steel surface. Here it is to be noted that nitrogen atom is coordinated to oxygen and hence no ion formation. Thus the film formation by the 2-PiNO inhibitor is supported by the increased linear polarization resistance compared to that with the blank corrodent medium and hence a reduced corrosion current with the inhibited corroding medium. The positive shift in the pitting potentials, in the presence of the inhibitor, indicates adsorption which retards pit nucleation. Also, in the presence of the inhibitor, significantly smaller pits were formed at the electrode surface compared to those formed in the solution without the inhibitor. The polarization values are presented in table 1.

Table 1 Corrosion parameters of mild steel immersed in presence and absence of inhibitors from potentiodynamic polarization study

| Medium (Blank/Inhibitor)	E_{corr} V vs SCE	b_a mV/dec	b_c mV/dec	LPR Ohm	I_{corr} mA
Blank(2N H_2SO_4)	-0.92	5.627	3.364	24	2.038
2-Picoline N-Oxide	-0.88	5.366	3.272	30	1.698
4-Picoline N-Oxide	-0.42	5.225	2.989	16	3.243

Table 2 Corrosion parameter of mild steel immersed in inhibited 2N H_2SO_4 a)2 PiNO b) 4 PiNO

| Sl. No.	System (Blank/Inhibitor)	R_{ct} (Ω)	C_{dl} (Farad)	Impedance Ω
1	Blank(2NH_2SO_4)	30	0.03185	0.68
2	2 Picoline N - Oxide	46	0.0300	1.33
3	4 Picoline N - Oxide	19.8	0.0316	1.32

4. Electrochemical impedance studies

Double layer capacitance values (C_{dl}) and charge-transfer resistance values (Rct) were obtained from impedance measurements. For Nyquist plots (Fig 5) it is clear that the impedance diagrams contain semicircle with centre under real axis. The size of the semicircle increases with the inhibitor concentration, indicating the charge transfer process as the main controlling factor of the corrosion of steel. It is apparent from the plot that

the impedance of the inhibited solution has increased with the increase in the concentration of the inhibitors. The experimental result of EIS measurements for the corrosion of mild steel in 2N H_2SO_4 in the absence and presence of inhibitors is given in Table 2. As it can be observed from the table, the charge-transfer resistance values (Rct) increased with increase in the concentration of the inhibitor whereas values of the capacitance of the interface (C_{dl}) starts decreasing, with increase in inhibitor concentration, which is most probably due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer. This suggests that the inhibitor acts via adsorption at the metal/solution interface and the decrease in the C_{dl} values is caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the electrode surface, which decreases the extent of metal dissolution. The higher values of charge transfer resistance (R_{ct}) and lower value of double layer capacitance (C_{dl}) observed with the inhibited corroding medium preferably the 2-PiNO isomer is attributed to the film formation by the inhibitor 2-PiNO at the metal surface leading to the inhibition of corrosion.
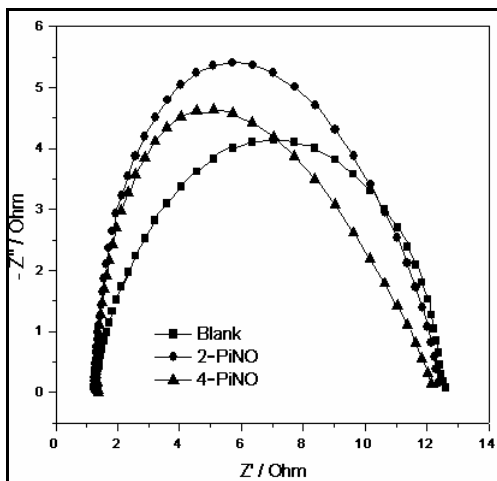
Fig 5. Nyquist plot of mild steel immersed in (a) 2N H_2SO_4 (b) 2N H_2SO_4 + 2-PiNO c) 2N H_2SO_4 +4-PiNO
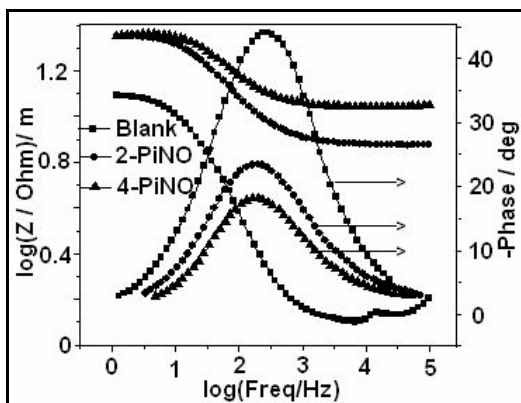
Fig.6. Bode plots for mild steel in (a) 2N H_2SO_4 (b) 2N H_2SO_4 +2-PiNO and (c) 2N H_2SO_4 +4-PiNO

From the Bode plots fig 6 same constant is obtained for the two inhibitors 2-PiNO&4-PiNO which envisages the function of a protective film of inhibitor on to the steel surface in the range of optimal concentrations, beyond which film degradation starts (20).

5. Adsorption isotherm studies

Adsorption isotherms are often shown to demonstrate the performance of organic adsorbent type inhibitors and important in determining the mechanisms of organic electrochemical reactions. The most frequently used adsorption isotherms are Langmuir, isotherms which describe the relation between surface coverage (θ) and the bulk concentration (ppm or mM) (21). Langmuir isotherm is found to fit best with the adsorption behaviour of the investigated 2-PiNO and 4-PiNO as evident from straight line plot obtained when

C/θ is plotted against C as shown in figure 7&8. It is evident from the figures that C/θ increases with concentration but decreases with increased immersion time. It indicates that the adsorption of the inhibitor onto the metal surface tends to be completed in one hour of immersion and thereafter the formed ferrous ions on the steel surface interfere with the value of C/θ.
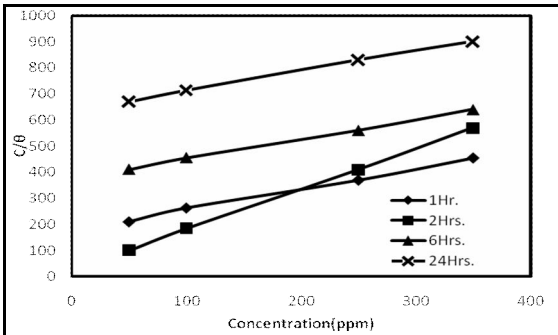

Fig 7. Langmuir adsorption isotherm of 2-PiNO in 2N H₂SO₄
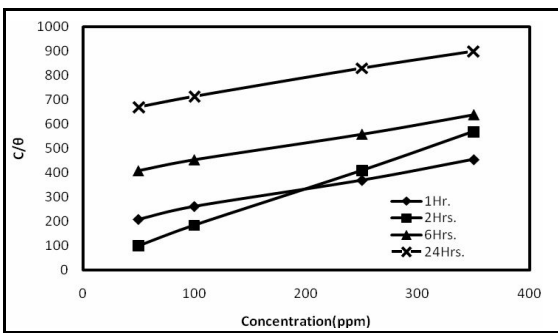

Fig 8. Langmuir adsorption isotherm of 4-PiNO in 2N H₂SO₄
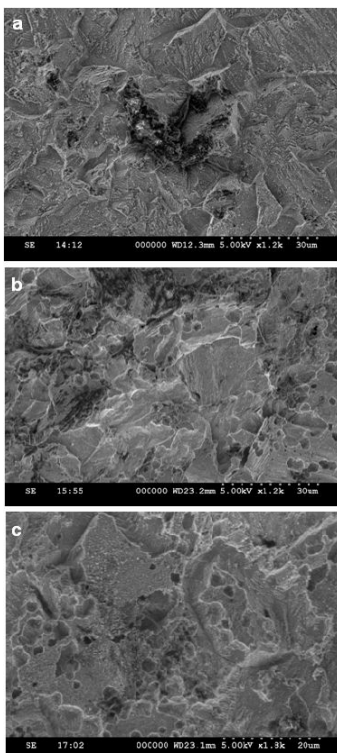
6. Scanning Electron Microscopy(SEM)

Fig 9. SEM image of mild steel specimen in (a) 2N H₂SO₄ without inhibitor (b) 2 N H₂SO₄ + inhibitor 2-PiNO (c) 2N H₂SO₄ + inhibitor 4-PiNO

Surface examination using SEM was carried out to study the effect of these inhibitors on the surface morphology of the mild steel specimen. Fig. 9.(a), (b) and (c) respectively denote the SEM images of mild steel blank specimen in 2N H_2SO_4 without inhibitor, in 2 N H_2SO_4 with the inhibitor 2-PiNO and in 2N H_2SO_4 with the inhibitor 4-PiNO. Fig 11(a) shows the polished surface of stainless steel after exposed to the testing environment, it was observed as a uneven surface along with the presence of dark spots. From the figures 11(a), 11(b) and 11(c), it is evident that the specimen surface is most damaged in the absence of the inhibitor and reasonably less damaged and even appears to be more polished in the presence of inhibitors. This is in accordance with the previous literature. It reveals that an adsorptive film of inhibitor is formed on the mild steel surface, which suppresses further corrosion and hence serves the inhibition function.

Conclusions

1. The synthesised compounds – 2PiNO and 4-PiNO function better towards the inhibition of corrosion of mild steel in 2N H_2SO_4.
2. The Inhibition efficiency of the substances under test, increases with the concentration of the inhibitors in the selection range.
3. Among the two isomeric nitrones tested, 2-PiNO performs better as a corrosion inhibitor than the isomer 4-PiNO which may be attributed to the better adsorption by the ionic form of the nitrone (N^+ -- O^-) to the Fe^{2+} ions formed initially on the mild steel surface due to the slight onset of corrosion.
4. Both compounds are act as good anodic inhibitors. This is proved from polarization studies.
5. Electrochemical impedance spectroscopy also confirm good inhibiting efficiency for 2-PiNO.
6. Surface morphology also shows good aggregation for anticorrosion behaviour of steel on inhibitors in 2N sulphuric acid medium.

Acknowledgement

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