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## Quinoline as corrosion inhibitors for mild steel: An Overview

**K.Lavanya** GokarajuRangaraju Institute of Engineering and Technology, Hyderabad, India Iavan5888@gmail.com

#### J.Saranya

GokarajuRangaraju Institute of Engineering and Technology, Hyderabad, India

## ABSTRACT

Traditionally, controlling of corrosion has been managed by various methods like cathodic protection, process control, reduction of the metal impurity content, and application of surface treatment techniques, as well as incorporation of suitable alloys. However, the use of corrosion inhibitors has proven to be the easiest and cheapest method for corrosion protection and prevention in acidic media. These inhibitors slow down the corrosion rate and thus prevent economic losses due to metallic corrosion on industrial vessels, equipment, or surfaces. Many researchers have recently focused on corrosion prevention methods using organic inhibitors for mild steel in acidic solutions to mimic industrial processes. This paper provides an overview of types of corrosion, corrosion process, and mainly recent work done on the application of quinolone derivatives as corrosion inhibitors for mild steel.

Keywords: Quinoline, Inhibitor, mild steel, acid medium, corrosion, alloy, cathodic protection, polarization, Impedance, adsorption.

## INTRODUCTION

Corrosion is a process in which loss of essential properties of material occurs as a result of its interaction with surroundings. In spite of remarkable advancement in the field of corrosion science and technology, the phenomenon of corrosion remains a major obstacle for industries all over the world [1]. Mild steel, also known as low carbon steel, the most common form of steel because of its low price and good material properties those are acceptable for many applications. Industrial processes such as acid cleaning, pickling, descaling, and drilling operations in oil and gas exploration use acidic solutions extensively and as such iron and steel vessels or surfaces used in these environments are prone to corrosion [2]. However, the challenge is that it has low corrosion resistance in acidic environments. Use of corrosion inhibitors is one such best available method to minimize the loss of steel. For this purpose, the organic compounds containing N, P, S, and O in their molecular structures have proven as efficient candidates as corrosion inhibitors [3]. This paper summarizes the corrosion inhibition of quinoline derivatives as inhibitors on different metal surfaces such as mild steel, carbon steel, steel, copper, etc., in different medium such as sulphuric acid, hydrochloric acid, nitric acid, formic acid, sodium chloride, etc.,. The information presented in this review is useful for diverse industrial fields and for other applications where corrosion inhibitors for mild steel materials are needed.

## EXPERIMENTAL PROCEDURE

Erdogan et al., investigated the adsorption and corrosion inhibition properties of some novel quinoline derivatives namely, 2-amino-7-hydroxy-4-phenyl-1.4-dihydroquinoline-3-carbonitrile (Q1), 2-amino-7-hydroxy-4-(p-tolyl)-1,4-dihydroquinoline-3-carbonitrile (Q2), 2-amino-7-hydroxy-4-(4methoxyphenyl)-1,4-dihydroquinoline-3-carbonitrile) (Q3) and 2-amino-4-(4-(dimethylamino)phenyl)-7-hydroxy-1,4-dihydroguinoline-3-carbonitrile (Q4) on the corrosion of iron using guantum chemical and molecular dynamics simulation approaches. The relationship between corrosion inhibition and global reactivity descriptors such as  $E_{HOMO}$ ,  $E_{LUMO}$ , HOMO-LUMO energy gap ( $\Delta E$ ), chemical hardness (n), softness ( $\sigma$ ), electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), electrophilicity ( $\omega$ ), nucleophilicity ( $\epsilon$ ), electrons transferred from inhibitors to metal surface ( $\Delta N$ ), initial molecule–metal interaction energy ( $\Delta \psi$ ), total electronic energy (E), the energy change during electronic backdonation process ( $\Delta E_{b-d}$ ) were provided by quantum chemical calculations. The adsorption behavior of studied inhibitors on Fe (110) surface was investigated with the help of molecular dynamics simulation approach. The adsorption efficiency on Fe (110) surface of the quinoline derivatives followed the order: Q4 > Q3 > Q2 > Q1. Experimental results were in good agreement with theoretical studies [4].

Fouda et al., tested the efficiency of 5-(3,4-dimethoxyphenyl)-8,10-dimethoxy-1,3-dimethylpyrimido-[5,4-c]quinoline-2,4-dione(PQD) as a corrosion inhibitor for Cu and  $\alpha$ -brass in 1M HNO<sub>3</sub> by weight loss and electrochemical techniques such as potentiodynamic polarization, electrochemical impedance spectroscopy and electrochemical frequency modulation techniques. The calculated adsorption thermodynamic parameters indicated that the adsorption was a spontaneous, exothermic process. The adsorption of the PQD on the Cu and  $\alpha$ -brass surfaces in the acid solution was obeyed Langmuir's adsorption isotherm. Scanning electron microscope (SEM) results proved PQD is forming a protective film on the Cu and  $\alpha$ -brass surfaces [5]. Sundaram et al., investigated the effect of quinoline nucleus based pharmaceutically active compound 5-Nitro- 8-Hydroxy Quinoline (NHQ) against the corrosion of mild steel in 1M HCl solution by weight loss and electrochemical (Tafel polarization, Linear polarization and Electrochemical impedance spectroscopy) techniques. From all the four methods, it is inferred that inhibition efficiency increases with increasing the inhibitor concentration from 50 to 300 ppm. The adsorption behavior of inhibitor obeyed Langmuir adsorption isotherm. Thermodynamic parameters were also calculated and predicted that the process of inhibition is a spontaneous reaction. EIS technique exhibits one capacitive loop indicating that, the corrosion reaction is controlled by charge transfer process. Tafel polarization studies revealed that the inhibitor is of mixed type and the mode of adsorption is physical in nature. FT-IR, SEM and EDX techniques were performed to study the surface morphologies[6].

He also used weight loss, electrochemical, scanning electron microscopy and energy dispersive Xray spectroscopy (EDX) methods to examine the corrosion inhibition performance of quinoline-8sulphonyl chloride (QSC) on mild steel in 1 M H<sub>2</sub>SO<sub>4</sub>solution. The corrosion rate decreased with increase in inhibitor concentration. QSC proved as a good corrosion inhibitor for mild steel in acid solution, by weight loss & electrochemical studies. QSC acted as a mixed inhibitor was showed by Tafel plots. The adsorption of the used inhibitor obeyed Langmuir adsorption isotherm. The formation of protective film on the surface of mild steel was confirmed by SEM and EDX techniques

Priyanka Singh et al., were used weight loss, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarizations methods to analyze the corrosion mitigation effect of quinoline derivatives such as 2-amino-7-hydroxy-4-phenyl-1,4-dihydroquinoline-3-carbonitrile (Q-1), 2-amino-7-hydroxy-4-(p-tolyl)-1,4dihydroquinoline-3-carbonitrile(Q-2),2-amino-7-hydroxy-4-(4-

methoxyphenyl)-1,4dihydroquinoline-3carbonitrile(Q-3),2-amino-4-(4-(dimethylamino)phenyl)-7hydroxy-1,4-dihydroquinoline-3-carbonitrile (Q-4) using. Q-4 showed the maximum inhibition efficiency of 98.09% at 150 mg/l among all the investigated inhibitors. Corrosion inhibition took place due to the adsorption of inhibitor molecules on the metal surface, was proved by electrochemical impedance spectroscopy measurements. The show that Q-1, Q-2, Q-3 were proved as a mixed-type inhibitor while Q-4 acts as a cathodic inhibitor by potentiodynamic polarization measurements. The adsorption of quinoline on mild steel surface obeyed the Langmuir adsorption isotherm. The corrosion inhibition occurs due to the adsorption of the inhibitor molecules at the metal/solution interface was confirmed by the surface analysis techniques (SEM/AFM/XPS) [8].



Figure1:Pictorial representation of adsorption of one of quinoline derivatives on MS surface in 1M HCI.

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Verma et al., has investigated inhibition efficiencies of 2-amino-4-(4-nitrophenyl) guinoline-3carbonitrile(AAC-1),2-amino-4-phenylquinoline-3-carbonitrile(AAC-2) and 2-amino-4-(4hydroxyphenyl)guinoline-3-carbonitrile (AAC-3) of mild steel corrosion in 1M HCl using weight loss, electrochemical potentiodynamic polarization and electrochemical impedance spectroscopy, surface (SEM, EDX and AFM) and quantum chemical calculation methods proved that AACs exhibited good inhibition efficiency against the corrosion of mild steel in acidic solution. The inhibition efficiency of AACs is in the order of AAC-3 (96.52%), AAC-2(95.65%) and AAC-1 (94.78%). Furthermore, it was revealed that AACs act as cathodic inhibitor by potentiodynamic polarization study. Inhibition efficiencies were enhanced with an increase in the concentration of 2-amino-4arylquinoline-3-carbonitriles (AACs) was suggested by weight loss and electrochemical results. AACs adsorb on a mild steel surface and it obeyed the Langmuir adsorption isotherm. The filmforming ability of AACs on the mild steel surface was revealed by SEM, EDX and AFM studies. Mechanistic insight into the mechanism of inhibition action of AACs was provided by quantum chemical calculations. It was concluded that the presence of electron releasing hydroxyl (-OH) groups in AAC-3 increase the inhibition efficiency whereas electron withdrawing nitro  $(-NO_2)$  groups in AAC-1 decrease the inhibition efficiency based on the experimental and theoretical studies [9].

Wang et al., examined the corrosion protection effect of two quinoline derivatives [10], 8aminoquinoline (8-AQ) and 8-nitroquinoline (8-NQ), on AA5052 aluminum alloy in 3% NaCl solution. 8-AQ and 8-NQ were anodic inhibitor and retard the anodic electrochemical process. 8-AQ and 8-NQ form a protective film on the AA5052 alloy surface shown by SEM/EDS analysis confirmed that there is a formation of strong hybridization between the p-orbital of reactive sites in the inhibitor molecules and the sp-orbital of the AI atom confirmed by density functional theory (DFT) calculation.

Sourav et al., investigated the mechanism of corrosion inhibition on mild steel surface of two mercapto-quinoline Schiff bases, namely 3-((phenylimino)methyl)quinoline-2-thiol(PMQ)and3-((5-methylthiazol-2-ylimino)methyl)quinoline-2-thiol (MMQT) is by quantum chemical calculation and molecular dynamics simulation. They investigated the relative corrosion inhibition performance by quantum chemical parameters such as  $E_{HOMO}$ ,  $E_{LUMO}$ , energy gap ( $\Delta E$ ), dipole moment ( $\mu$ ), electronegativity( $\chi$ ),global hardness( $\eta$ ) and fraction of electron transferred from the inhibitor molecule to the metallic atom surface( $\Delta N$ ) studies [11]. Fukui indices used to analyze parameters like local reactive sites of the inhibitor molecules. Moreover, molecular dynamic simulation analyzed that the adsorption behavior of the inhibitor molecules on Fe (110) surface. The binding strength of the inhibitor molecules on mild steel surface followed the order MMQT>PMQ.

Zhao et al., investigated the corrosion inhibition of a quinolinium quaternary ammonium salt and a Gemini surfactant, 1,3-bis (dodecyl di methyl ammonium chloride)-2-propanol, for mild steel in  $H_2S$  and  $CO_2$  saturated brine solution by using polarization test, EIS and XPS. The synergistic effect was found between these two compounds when the Gemini concentration is less than 50 mg/lt in the solution containing 100 mg/lit quinolinium quaternary ammonium salt, and it disappears when the Gemini concentration is larger than 50 mg/lit [12]. The synergistic mechanism is explained by competitive adsorption of these two compounds on steel surface.

Mahendra et al., synthesized two quinoline-thiazole derivatives namely, {4-[1-aza-2-(phenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2-chloro(3-quinolyl))vinyl] (Inh I) and {4-[1-aza-2-(4-methoxyphenyl)vinyl]-3-phenyl-2-thioxo(1,3-thiazoline-5-yl)}-N-[1-aza-2-(2 chloro (3quinolyl))vinyl] (Inh II) and used weight loss measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques to investigate the synthesized quinolinethiazole derivatives as an inhibitor for mild steel corrosion in 15% HCl solution.

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The inhibitors Inh I and Inh II showed corrosion inhibition efficiencies of 81.5% and 84.0% at 20 ppm concentration and 95.0% and 96.3% at a 200 ppm concentration, respectively, at 333 K. The inhibition efficiency of both the inhibitors was found to be increased with an increase in temperature and concentration of inhibitors. Polarization studies revealed that both the studied inhibitors are of mixed type in nature. The adsorption of inhibitors on the mild steel surface obeyed the Langmuir adsorption isotherm. The surface study of uninhibited and inhibited mild steel sample using scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed. The semi-empirical AM1 method was employed for theoretical calculations [13].





corrosion inhibition of mild steel in the absence and presence of different concentrations of mercaptoquinoline derivatives namely, 3 (phenylimino)methyl) quinoline-2-thiol(PMQ) and 3-((5methylthiazol-2vlimino)methyl)quinoline-2-thiol (MMQT), of mild steel in 1 N HCl solution by using conventional weight loss, potentiodynamic polarization, linear polarization, electrochemical impedance spectroscopy, and scanning electron microscopic studies. It was found that PMQ and MMQT were effective inhibitors and their inhibition efficiency was significantly increased with increasing concentrations of inhibitors, by weight loss and electrochemical measurements. The evaluated PMQ and MMQT both acted as mixed inhibitors, showed by polarization curves. The adsorption of these inhibitors on the mild steel was found to follow the Langmuir adsorption isotherm. Results confirmed that the rate of corrosion of mild steel increased with increasing temperature over the range 25°-45°C both in the presence and in absence of inhibitors. Activation energies in the presence and absence of PMQ and MMQT were obtained [14].

He investigated the corrosion inhibition of mild steel (MS) in 1N HCl solution in presence of two quinoline derivatives, viz. 2-chloro quinoline 3-carbaldehyde(CQC) and (2-chloro-quinoline-3ylmethyl)- p-tolyl-amine (CQA) using conventional weight loss, potentiodynamic polarization, linear polarization and electrochemical impedance spectroscopy [15]. It was proved that CQQC and CQA are efficient inhibitors of corrosion, as the losses in weights of mild steel sample have reduced. Electrochemical polarization studies confirmed that the inhibitors showed the mixed mode of inhibition. The results of electrochemical impedance spectroscopy have showed changes in the impedance parameters like charge transfer resistance and double-layer capacitance. It was assumed that the inhibition action of these compounds occur via adsorption on the steel surface through the active centers contained in the molecules. The experimental results complemented furthermore by quantum chemical calculations at B3LYP/6-31G (d, p) level.

## CONCLUSIONS

Corrosion inhibition study on various metals in various environments with quinoline derivatives as inhibitors at room and higher temperatures have been reviewed. Electrochemical studies, surface morphology and computational studies like quantum chemical studies and molecular dynamic simulation have been reviewed. Variousadsorption isotherms have been analyzed. This review will be useful for corrosion inhibitor research where conditions are not so severe, e.g., acid pickling, industrial cleaning, and acid descaling.

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