

## ABSTRACT

Corrosion is defined as spontaneous destruction or deterioration of metals and alloys due to chemical or electrochemical reactions when they come into contact with an environment containing corrosive agents. Due to their high thermal and electrical conductivity, copper and copper-based alloys are widely used in a great variety of applications, such as industrial equipments, building construction, electricity, electronics, chemical, coinages, ornamental parts, etc. Copper is exposed to acid media during acid pickling, in cleaning of oil refinery equipment and heat exchangers and in oil well acidizing etc.

The use of inhibitors is one of the most practical methods for protection against corrosion. The inhibiting mechanism is generally explained by the formation of a physical and/or chemical adsorption film on these metal surfaces. It is well known that organic compounds act as inhibitors due to delocalized  $\pi$ -electrons and due to the presence of hetero atoms such as sulphur, nitrogen and oxygen.

In the present work, corrosion inhibitive properties of some fluoroquinolones namely ciprofloxacin, norfloxacin, ofloxacin, sparfloxacin on the corrosion of copper in nitric acid and sulphuric acid media are investigated. Their corrosion inhibitive properties were evaluated employing different methods such as weight loss, potentiodynamic polarization, impedance spectroscopy and quantum chemical studies.

Weight loss measurements showed an increase in inhibition efficiency with concentration and an efficiency of about 95 % is achieved at concentration of 1 mM in both the media. The impedance studies revealed

that  $R_{ct}$  values increased with increase in inhibitor concentrations in both the media which is a result of an increase in the surface coverage by the inhibitor. The decrease in  $C_{dl}$  is due to the adsorption of the inhibitor molecule with water replacement at the metal/ solution interface resulting in a decrease in local dielectric constant and an increase in thickness of the double layer. The potentiodynamic polarization curves indicated that these compounds acted as a mixed type of inhibitor.

The potentiodynamic polarization studies were carried out in the absence and in the presence of the inhibitors in both the media at 308 K, 318 K and 328 K and thermodynamic parameters such as  $E_a$ ,  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  have been determined. There is an increase in inhibitor efficiency with rise in temperature, due to chemisorption and in turn to a higher surface area coverage leading to a decrease in the rate of dissolution. The  $\Delta G_{ads}$  values are negative revealing the spontaneity of the adsorption processes and the stability of the adsorbed layer on copper. The decrease in  $E_a$  with the addition of inhibitors in both the media revealed that the inhibitor molecules are adsorbed onto the metal surface by chemisorption. The negative value of  $\Delta H$  indicates that the adsorption is an exothermic process.

The adsorption of these inhibitors on copper surface is found to obey Langmuir adsorption isotherm. From PZC measurements, the surface charge of copper at the OCP was found to be positive in the inhibited and uninhibited acid solutions. Hence these molecules are shown to get adsorbed on to metal surface through anion bridges. Combined inhibitory effect of halide ions ( $Cl^-$ ,  $Br^-$ ,  $I^-$ ) and the inhibitors on the corrosion of copper in the two acid media, investigated by impedance measurements, revealed the synergistic effect of  $I^-$  in both the media, whereas  $Cl^-$  and  $Br^-$  were antagonistic.

The surface morphology, studied by scanning electron microscopy (SEM), showed the reduction in corrosion in the presence of inhibitors. Quantum chemical calculations substantiate the inhibition efficiencies obtained from experimental results.